Chemical Contamination of Hamilton Harbour: A Review.

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CHEMICAL CONTAMINATION OF HAMILTON HARBOUR:

A REVIEW

by

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ABSTRACT

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The contamination of Hamilton Harbour with chemical wastes has increased since 1800, in parallel with industrial and urban growth. While improved waste treatment has reduced chemical inputs by more than 90% since 1960, storm sewer separation in Hamilton is incomplete and municipal and industrial discharges cause unacceptable conditions.

Loadings to the Harbour are quite high for Fe and Zn, relative to other Lake Ontario sources. Among organic materials, oil and grease is discharged in the largest volume, but it has little toxicological significance. Loadings of phenols, PAHs, pesticides, and PCBs are much smaller, particularly compared to sources such as the Niagara River.

Levels in water and sediment of metals, oil and grease, and PAHs are highest near the steel industries, the major source. PCBs are highest near a site where transformers were manufactured and in the Windermere Basin. In contrast, pesticides occur near combined sewer overflows and near tributaries draining urban areas.

Metals in water exceed background levels in Lake Ontario and, frequently, water quality objectives. Complexation may reduce toxicity but periodic effects on algae are possible. Sediments exceed dredge spoil disposal guidelines for As, Cd, Cr, Cu, Fe, Pb, Ni and Zn. Relative to offshore sediments, only Fe and Zn appear elevated but levels of all metals in both Harbour and offshore sediments exceed levels in sediments deposited before 1800.

Algae contain less Co, Zn, and Pb than associated sediments but benthic invertebrate communities are affected by sediment contamination and low dissolved oxygen. Benthic-feeding fish contain more Pb than pelagic feeders, suggesting that sediment metals are taken up. However, Pb levels in fish are lower than in other Lake Ontario locations; fish may be excluded from highly contaminated sediments by low dissolved oxygen levels. Hg in fish fillets is below the Provincial criterion for consumption, as were other metals. Hg, Pb and Cd levels in nesting gulls exceeded those in other locations, but the source is obscure since gulls feed both inside and outside the Harbour.

Average levels of PCBs in sediments are within the range of other Harbours on Lake Ontario but well above offshore sediments. Pesticide levels in sediments are quite low, similar to other Lake Ontario Harbours. Benthic worms in Windermere Basin were more contaminated with chlorinated organics than associated sediments but levels in fish fillets declined steadily between 1972 and 1981 and are lower than in Lake Ontario fish. Eggs from fish-eating birds nesting in Hamilton Harbour are highly contaminated; while levels declined after 1970, they are far higher than in fish due to biomagnification. Eggs of

and 1981 and are lower than in Lake Ontario fish. Eggs from fish-eating birds nesting in Hamilton Harbour are highly contaminated; while levels declined after 1970, they are far higher than in fish due to biomagnification. Eggs of snapping turtles are also quite contaminated, perhaps due to long-lived parents; except for PCBs, the levels are lower than in birds, implying a local source of PCBs.

PAHs in water are mostly associated with particulates which settle to the sediments or wash into Lake Ontario; sediments contain 10 - 100 times the levels in Lake Ontario. Levels in fish are similar to those of fish from the Detroit River and may contribute to a high prevalence of tumours.

Overall, chemical loadings to the Harbour remain unacceptably high. Benthos are directly affected but fish seem to be protected by low levels of dissolved oxygen; correcting oxygen problems may increase chemical contamination of fish and other biota. This review is limited by past analytical capabilities since no data were found on chemicals such as chlorinated dioxins. More than 60 'non-routine' organic chemicals were measured in effluents from the Hamilton and Burlington WTPs, including chlorinated compounds, PAHs, furans and phthalates. Research is required to describe the full extent of chemical loadings and contamination of the Harbour, suitable means of disposing of sediments or treating them in place, bioaccumulation of sediment chemicals, identification of all sources of PCBs, and assessment of the fate and effects of PAH.

RESUME

Harlow, H.E. et P.V. Hodson. 1988. Chemical contamination of Hamilton Harbour: A review. Can. Tech. Rept. Fish. Aquat. Sci. 1603, pp .
(Examen de la contamination chimique du port d'Hamilton)

La contamination du port d'Hamilton par les déchets chimiques augmente depuis 1800, parallèlement à la croissance industrielle et urbaine. Grâce à l'amélioration du traitement des déchets, on a pu réduire de 90% depuis 1960 les quantités de substances chimiques introduites dans le port, mais la séparation des égoutes pluviaux à Hamilton est incomplète et les déversements municipaux et industriels entraînent des conditions inacceptables.

On remarque dans le part des charges relativement élevées pour Fe et Zn par rapport aux autres sources du lac Ontario. Parmi les matières organiques, les rejets les plus volumineux sont ceux d'huiles et de graisses, mais ils n'ont qu'une faible toxicité. Les charges de phénols, de pesticides et de BPC sont beaucoup plus faibles, particulièrement à comparer à d'autres sources comme la rivière Niagara.

Dans l'eau et les sédiments, la concentration des métaux, des huiles et des graisses et des HAP est la plus élevée près des acriéries qui en sont la source principale. Les concentrations de BPC sont les plus élevées près d'un emplacement où l'on fabriquait des transformateurs et dans le bassin de Windermere. Les pesticides se trouvent surtout près des déversoirs de trop-plein du réseau unitaire et près des endroits où se jettent les affluents qui ont drainé les zones urbaines.

Dans l'eau, la concentration des métaux dépasse les concentrations de fond que l'on trouve dans le lac Ontario et fréquemment les objectifs quant à la qualité de l'eau. La complexation peut réduire la toxicité des métaux sans pour cela éliminer des effets périodiques sur les algues. Les concentrations dans les sédiments dépassent les lignes directrices en matière d'élimination des rejets de dragage pour As, Cd, Cr, Cu, Fe, Pb, Ni et Zn. Par rapport aux sédiments que l'on trouve au large, seuls Fe et Zn semblent présenter une concentration élevée. Toutefois, que ce soit dans le port ou au large, les celles relevées dans les sédiments déposés avant 1800.

Les algues contiennent moins de Co, de Zn et de Pb que les sédiments associés, mais les communautés d'invertébrés benthiques sont touchées par la concentration sédimentaire et la faible quantité d'oxygène dissous. Les poissons qui se nourrissent sur le fond contiennent plus de Pb que les prédateurs pélagiques, ce qui indiquerait que les métaux sédimentaires sont absorbés. Toutefois, les concentrations de Pb dans les poissons sont inférieures à celles que l'on a relevées dans d'autres emplacements du lac Ontario; les poissons peuvent ne pas être touchés par la contamination élevée des sédiments en raison de la faible quantité de Hg inférieure au critère provincial pour la consommation et il en est de même pour les autres métaux. Les concentrations de Hg, Pb et Cd dans les goélands en période de nidification dépassent celles que l'on a relevées ailleurs, mais il est difficile de déterminer la source en question puisque les goélands se nourrissent aussi bien à l'intérieur du port qu'à l'extérieur.

Les concentrations moyennes de BPC dans les sédiments sont de l'ordre de celles que l'on relève dans les autres ports du lac Ontario mais sont bien supérieures aux concentrations dans les sédiments sont basses comme dans les autres ports du lac Ontario. Les vers benthiques du bassin de Windermere sont plus contaminés par les maitières organiques chlorées que les sédiments qui leur sont associés, mais la concentration de ces matières dans les filets de poisson a diminué régulièrement entre 1972 et 1981 et elle est inférieure à la concentration dans les poissons du lac Ontario. Les oeufs des oiseaux pisciphages qui nichent dans le port d'Hamilton sont fortement contaminés. Après 1970, les concentrations de contaminants ont diminué mais elles sont bien supérieures aux concentrations relevées dans les poissons en raison de la bio-amplification. Les oeufs des chélydres serpentines sont aussi très contaminés, peut-être en raison de la longévité des parents, si ce n'est en ce qui concerne les BPC dont les concentrations sont inférieures à celles relevées dans les oiseaux, ce qui signifie qu'il existe une source locale de BPC.

Les HAP qui se trouvent dans l'eau sont sourtout associés aux particules qui se déposent dans les sédiments ou qui sont emportées dans le lac Ontario. Les sédiments contiennent entre 10 et 100 fois plus de HAP que ceux du lac Ontario. Les concentrations dans les poissons sont analogues à celles que l'on relève dans la rivière Detroit et sont peut-être responsables de la fréquence élevée des tumeurs.

Dans l'ensemble, les charges chimiques mesurées dans le port restent beaucoup trop élevées. Les benthos sont touchés directement, mais les poissons semblent être protégés en raison des faibles quantités d'oxygène risque d'augmenter la contamination chimique chez les poissons et dans la biote en général. Le présent examen est limité par les capacités des analyses passées puisque nous n'avons trouvé aucune donnée sur les substances chimiques comme les dioxines chlorées. Nous avons mesuré plus de 60 substances chimiques organiques non régulières dans les effluents des stations d'épuration des eaux d'Hamilton et de Burlington, y compris les composés chlorés, les HAP, les furannes et les phtalates. Il faut entreprendre des recherches pour décrire dans le détail les charges et la contamination chimiques du port, les moyens appropriés pour éliminer ou traiter sur place les sédiments, les méthodes d'élimination, la bio-accumulation des éléments chimiques dans les sédiments, la détermination de toutes les sources de BPC et l'évaluation du destin et des effets des HAP.

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1.0 INTRODUCTION

1.1 THE HARBOUR

Hamilton Harbour is at the west end of Lake Ontario. It is separated from the Lake by a natural sandbar cut by a shipping canal 107 metres wide and 10 metres deep (MOE, 1974). It is roughly triangular in shape with a length east to west of 8 km, a width north to south of 4 km, and an area of 22 km^2 (Fig. 1). The mean depth is 13 m with a maximum of 27 m in the central basin and there is extensive landfilling along the south shore. High rates of exchange of lake and Harbour water and large volumes of industrial and municipal effluents give relatively short retention times of about 0.25 years (MOE, 1985). The watershed drains 500 km^2 of industrial, residential and agricultural land.

Hamilton Harbour once had an abundant commercial fishery which declined dramatically after 1890 (Holmes and Whillans. 1984), due in large part to deteriorating water quality (Whillans, 1979). The Harbour is now most noted for having Canada's largest steel industries on its south shore, the Steel Company of Canada (STELCO) and the Dominion Foundry and Steel Company (DOFASCO), plus numerous other heavy industries. Because of industrial and municipal pollution, the Harbour has been identified by the Great Lakes Water Quality Board of the International Joint Commission as one of 42 areas of concern in the Great Lakes (IJC, 1985).

The purpose of this report is to review the discharge of metals and organic chemicals to Hamilton Harbour and their levels in water, sediment, and biota. Depletion of dissolved oxygen and increased levels of nutrients and ammonia have been reviewed elsewhere (Threader et al., 1987). A glossary of technical terms is presented in Appendix A.

1.2 SOURCES OF CHEMICALS

1.2.1. Industry

Industrialization of the Hamilton area began around 1835-45 with the opening of several iron foundries. The iron and steel industries became quite large, aided by factors such as railway expansion, agricultural booms, and the amalgamation of smaller industries to form STELCO and DOFASCO. Industries making iron and steel products, such as International Harvester, expanded in concert with the steel industry. Textile industries established in the 1850's were also active in Hamilton and Dundas until the 1950's (Weaver 1982).

Industrial discharges used to enter the Harbour's south shore waters. Before the construction of the Hamilton Wastewater Treatment Plant (WTP) in 1963, all industries discharged their wastes "through a complexity of private and municipally-owned sewer pipes" (OWRC 1967). Most industries were connected to the municipal WTP soon after its completion and the remainder joined by the late 1960's (MOE 1985). Presently, the two steel mills (STELCO and DOFASCO) are the only industries that still discharge some wastes directly to the Harbour. These include treated process effluents plus cooling and storm sewer water.

Wastes from Dundas, a town west of the Harbour (Fig. 1), enter Cootes Paradise, a marsh of approximately 2.45 km^2 (Lavender, 1986). Cootes Paradise drains into Hamilton Harbour at its west end.

Burlington and Waterdown, towns on the North Shore (Fig. 1), are not major industrial centres. About 3% of Burlington is zoned industrial (Snodgrass 1981) and all industrial effluents from Waterdown and Burlington are discharged to sanitary sewers.

1.2.2. Wastewater Treatment Plants

Municipal and industrial wastes are treated in Wastewater Treatment Plants in Hamilton, Burlington, Dundas and Waterdown. The Hamilton and Burlington plants discharge directly to the Harbour while the effluents from Dundas and Waterdown enter indirectly via Cootes Paradise and Grindstone Creek respectively (Fig. 1).

Hamilton's primary treatment plant started operating in 1963, was modified to secondary treatment in 1972, and expanded in capacity to 273,000 m^3/d in 1977. This plant requires no addition of chemicals for phosphorus removal (Craig et al. 1984) because steel industry wastes have sufficient iron content to precipitate phosphorus. It discharges 265,000 m^3/d of effluent to Windermere Basin (Craig et al. 1984).

The Burlington Skyway WTP is a secondary system with extended aeration. It discharges about 62,000 m^3/d to the Harbour's east end but its capacity is 93,000 m^3/d (Craig et al. 1984). It has been using ferric chloride to remove phosphorus since 1976 (MOE 1985).

The Dundas WTP was heavily overloaded in the early 1970's until an expansion was completed in 1978. It is a tertiary treatment plant for phosphorus removal and its effluent is discharged to Cootes Paradise. Waterdown's WTP also has tertiary phosphorus removal and its discharge is to Grindstone Creek, a tributary at the northwestern end of the Harbour.

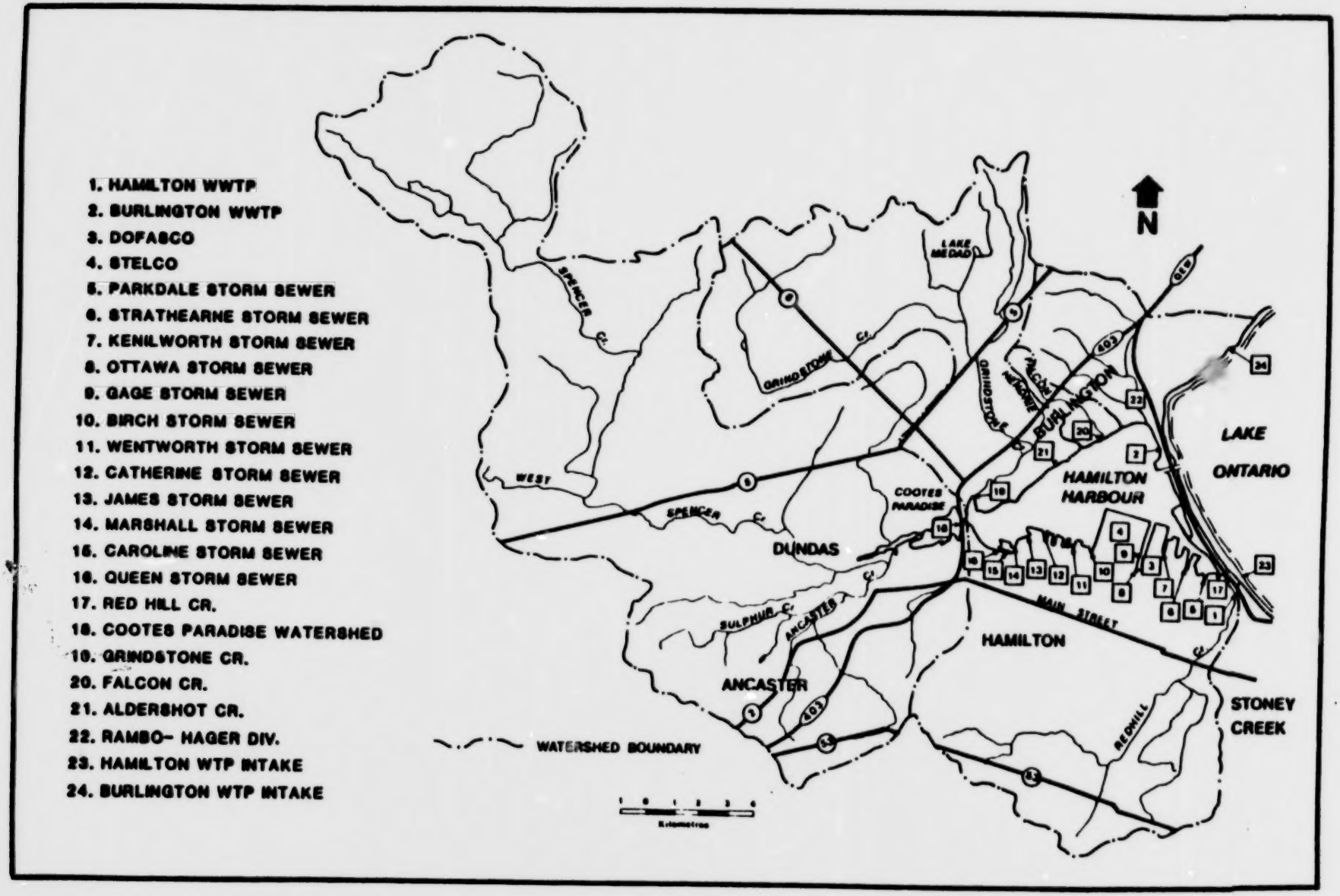

Figure 1. Hamilton Harbour showing watershed boundaries, major tributaries and sewers (from Snodgrass 1981)

1.2.3. Storm Sewers and Tributaries

Rainfall and spring runoff from Hamilton and Burlington enter Hamilton Harbour via storm sewers. Hamilton has a combined sewer system in most of the city; untreated sewage and stormwater overflows into the Harbour about 50 times per year during periods of high rainfall (S. Spencer, Hamilton Harbour Stakeholders Meeting, 1986). In Hamilton, overflows from above the escarpment drain into Redhill and Chedoke Creeks and those below drain directly to the Harbour through 20 major outfalls (MOE 1981, Holmes 1986). An ongoing project to separate sanitary and storm sewers is to be completed over the next 50 years at a cost of 60 million dollars (Spencer, 1986).

The major tributaries to Hamilton Harbour are Cootes Paradise outflow (which includes Spencer Creek), Redhill Creek, and Grindstone Creek. Each carries stormwater inputs that are not included in stormwater estimates.

In Burlington, all runoff in the watershed that drains to the Harbour enters small creeks or is discharged directly via storm stewers (Dalgarno, 1985). Therefore, the minor creeks of Burlington (Falcon, Indian and Aldershot Creeks) and the Rambo-Hager Diversion are considered storm water inputs for the purpose of this report. Since Indian Creek drains into the Rambo-Hager, their combined input will be referred to hereafter as Rambo-Hager loading which also includes some storm water from central Burlington.

1.2.4. Non-point Sources

There are 5 non-point sources of chemicals to Hamilton Harbour: shipping, spills, atmospheric inputs, contaminated groundwater from landfill and resuspension of sediments.

1.2.4.1. Shipping

Hamilton Harbour was opened to large ships with the completion of the Burlington Canal in 1827. In 1984, 682 commercial vessels carrying a cargo of 12.33 million tonnes used the Harbour during its navigation season, April 1 - December 20, (Edwards 1985). Bulk movements included coal, iron ore, sand, steel scrap and petroleum products (Canadian Ports & Seaway Directory 1985). Although not on the coast, Hamilton ranks among Canada's leading seaports in total cargo tonnage handled.

Types of shipping wastes that may pollute the Harbour include:

1. bilge water - drainage collected in the lower part of the vessel from internal waste sources: includes sanitary wastes, lubrication oils etc. (IJC 1969b);
2. ballast water - pumped into fuel or ballast tanks to maintain empty vessel stability (IJC 1969b); ballast water may contain fuel;
3. accidental discharges of cargo or fuel tanks;
4. wash water from the decks of bulk carriers.

These discharges remain largely unquantified except for tanker spills.

1.2.4.2. Spills

Spills are a frequent source of chemicals, including both inorganic and organic materials (see section 3.4.2., Table 20). Records of spills are maintained by Environment Canada but it is likely that some spills are not reported. The majority of spills are from industrial accidents on land owned by industry or occur during transportation. Most material spilled on land but not cleaned up at the site would enter sewers and be treated at the WTP. In the four years reported, 17 of 35 spills (50%) were cleaned up partially or completely. The fate and chemical composition of materials spilled in water was unknown.

1.2.4.3. Atmosphere

Air pollution is a potential source of chemicals to the Harbour, both as direct wet or dry deposition and as material washed from the watershed. Deposition on land is included in tributary loadings; while its relative contribution to Harbour contamination is unknown, it is at least accounted for. In contrast, direct inputs to the Harbour's surface cannot be measured since there is no routine monitoring of precipitation. Some estimates can be made from dustfall surveys and some isolated research projects (e.g. see section 3.4.3.). However, these estimates are rather rough since wind direction, wind strength and conditions relating to the source and properties of each chemical will affect the ultimate destination of local material.

The major local sources of air pollutants are Hamilton's industries, the Solid Waste Reduction Unit (SWARU incinerator), the Hamilton WTP sludge incinerator, and automotive emissions.

The Harbour is also flanked by two major automobile routes, the Burlington Skyway Bridge and Queen Elizabeth Way on the east end, and Highway 403 on the west end (Fig. 1). Each route crosses a narrow sandbar between the Harbour and either Lake Ontario or Cootes Paradise. Both routes are elevated, which may increase dispersal of automotive pollutants.

1.3. MATERIALS AND METHODS

1.3.1. Data Sources

Historical data on wastes and water quality were obtained through Hamilton Municipal Laboratory Annual Reports and Ontario Water Resources Commission Reports. The bulk of recent data on water, sediment and effluent quality was supplied by the Ontario Ministry of the Environment (MOE) in the form of published and unpublished reports. Additional data on contaminants in sediments and sediment composition were supplied by Mr. V. Cairns, Department of Fisheries and Oceans. MOE also supplied the majority of data on contaminants in fish from its sportfish testing program. Supplemental data on contaminants in other biota came from Dr. Chip Weseloh and Mr. John Struger of

the Canadian Wildlife Service, and Fisheries and Oceans unpublished reports. Information on Wastewater Treatment Plants came from the Wastewater Technology Centre (WTC) at the Canada Centre for Inland Waters (CCIW) in Burlington. Atmospheric data were also obtained from CCIW personnel. Municipal landfill information came from personnel of the City of Burlington, the Halton Regional Government and consultants' reports.

All other unpublished information came from personal communication with industry, government and municipal employees (see Acknowledgments, Section 21.0.).

1.3.2. Data Analysis

For this report, the Harbour was divided into six areas: South Shore (SS), East End (EE), Central Basin (CB), North Shore (NS), West End (WE) and Windermere Basin (WB) (Fig. 2). The divisions were made on the basis of shoreline use, pollution sources and depth.

Sampling stations from various data sets were transposed into the areas using a Zoom Transfer Scope if a scaled map was provided by the authors. Hamilton Municipal Laboratory maps were transposed using visible shore markers and the results verified by personal communications with lab personnel. Area means were calculated for values from all stations within each zone.

Due to very large ranges within data sets, variances were usually non-homogenous. Hence geometric means were calculated in all cases where raw data were available. For metals and phenol in water, area means were calculated only when four or more samples were available at a sampling station. Data were more limited for metals in sediments so that all available data were used for yearly or area trend analyses.

No month-to-month trends for metals in water were evident for any metal, so all months with >4 samples/month were averaged. Since bacterial degradation of phenols may vary with temperature, only August means were used for a consistent year-to-year trend analysis.

For atmospheric sources of pollution, no loading figures were calculated due to a lack of data although some rough estimates were made to provide perspective. Loadings to the atmosphere were also provided for perspective. Where atmospheric loadings were not available, the concentrations emitted were shown.

Point sources of chemicals were defined as discrete inputs that could be easily sampled, in contrast to diffuse sources such as the atmosphere. For the purpose of this paper, tributaries and storm sewers were considered point sources of contaminants to the Harbour.

Data for biota were not separated into areas except for organisms known to be sedentary (e.g. oligochaetes).

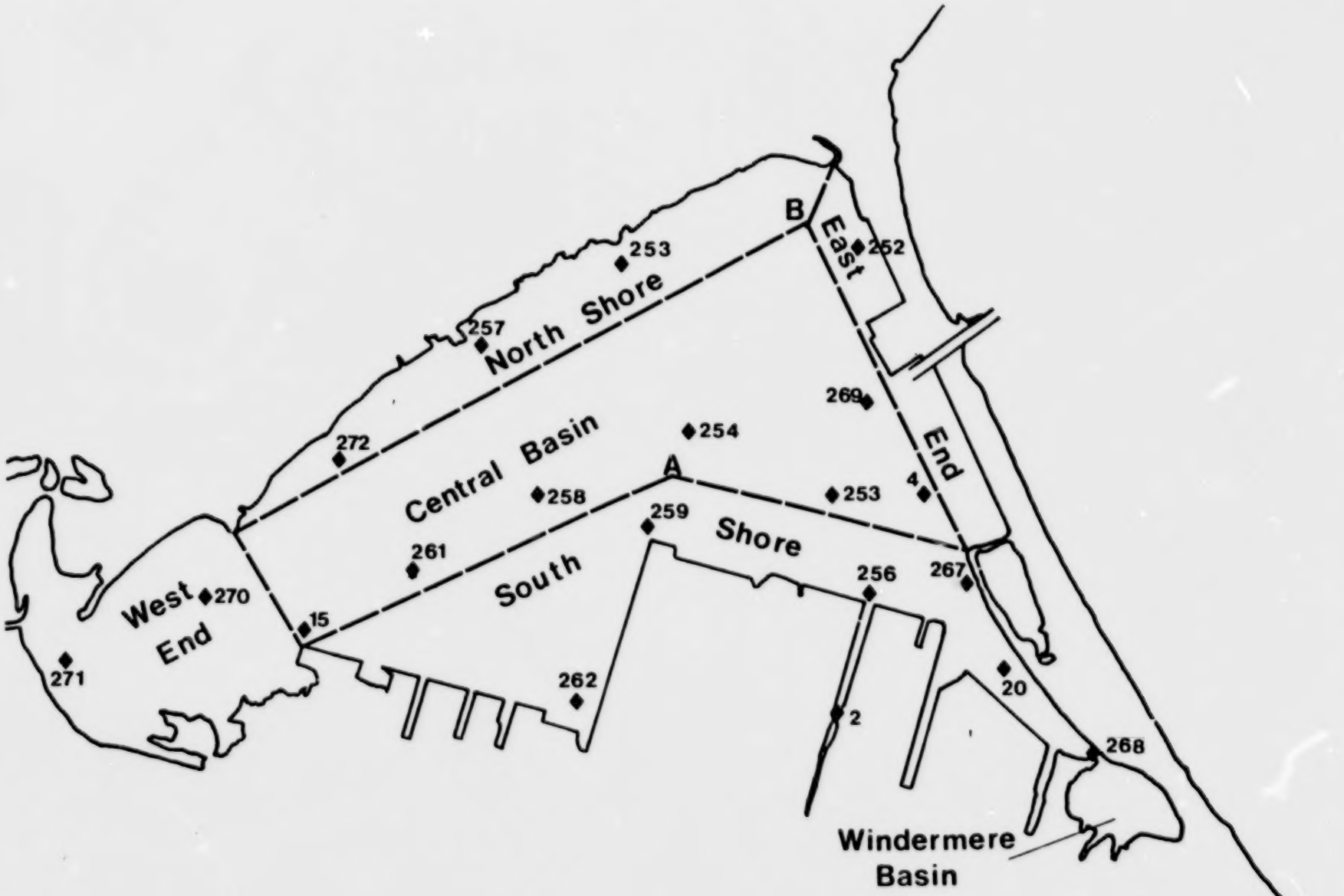

Figure 2. Designated zones of Hamilton Harbour showing sampling stations commonly used by the Ontario Ministry of Environment. Zone intersections (Points A and B) were located at: A (L48°17'18"N, λ79°49'21"W) and B(L43°18'40"N, λ79°48'50"W).

1.3.3. Data Quality

In sediments, chemical concentrations are affected by particle composition and percent water in wet sediment. In the Harbour, lack of these data made the temporal and spatial comparisons of chemical levels less certain. The small number of analyses, especially in the east end and north shore areas, also limit the description of the Harbour.

Estimates of the loading of chemicals to the Harbour from industry have been made since 1964. However, the accuracy of these estimates from the 1960's and early 1970's is not known because no indication was given of the number of samples on which loading estimates were based. Since 1980, effluents were sampled weekly by DOFASCO and bimonthly by STELCO (Matchette 1986). Therefore, comparisons of current loadings to a 1964 base should be treated with caution.

The methods used by the Hamilton Municipal Laboratories to determine the levels of phenols and iron in Harbour water from 1958 to 1970 are in Standard Methods, beginning with the 9th edition. Phenol was measured by the 4-aminoantipyrene method which detects all phenols except those substituted in the para position by alkyl, aryl, nitro, benzoyl, nitroso or aldehyde groups (APHA 1980). Iron was determined colorimetrically using the salicylic acid method (HML 1960). No mention of this method was made in the 9th, 12th or 15th editions of Standard Methods (APHA 1946; 1965; 1980). Appropriate controls and blanks were always conducted and all results were reproducible (Forde 1986).

Only limited analyses of data on chemicals in biota can be undertaken due to a lack of standardized methods. No comparisons were made between fillet and whole fish samples but comparisons of samples expressed on a wet or dry basis were made by assuming a moisture content of 80%.

2.0 METALS AND CYANIDE IN HAMILTON HARBOUR

The major sources of metals and cyanide to Hamilton Harbour are industries, municipal WTPs, tributaries, stormwater runoff and non-point sources. The non-point sources include shipping, spills, atmospheric input, landfill leachate and resuspended sediments within the Harbour (Holmes 1986).

2.1 INDUSTRIAL LOADINGS

2.1.1. Direct Discharge

Though industrial discharges to Hamilton Harbour began over a century ago, inputs have only been measured intermittently from 1964 to present (Table 1). Discharges from industries other than the steel mills are included in the Hamilton WTP effluent after 1967 (see section 3.0). Of the total industrial discharges of iron and cyanide in 1964 and 1967, the majority is from the steel industries; "other industries" accounted for only 0.46% and 0.22% respectively (Table 1). Total metal loadings from all industries prior to 1960 are unknown and cannot be dismissed as insignificant.

Table 1. Industrial loadings of metals and cyanide (kg/d).

Year	1964	1966	1968	1972	1973	1976	1977	1978	1979	1980	1982	1983	1984	1985
STELCO														
Iron	39540	24208	22317	9027	4990	10886	21500	4455	3709	11029	6300	4630	5575	2752
Zinc				454	953		990	510				64	171	72
Chromium		47		59	36		31	14			27			
Arsenic														
Copper							110	69			8			
Lead							15	23			27			
Cadmium							0							
Manganese							350	142						
Cyanide	1483	480	286	590	1497	181	1050	49	937	308	240	99	152	46
DOFASCO														
Iron	24494	34836	20408	11567	3254	4536	13000	2093	7973	6804	4030	2470	3550	2504
Zinc				957	546		110	137			73	54	95	56
Chromium			82	68	92		58	22						
Copper							23	27						
Lead							7	41			4			
Cadmium							0							
Manganese							220	60						
Cyanide	454	204	463	98	39	136	40	55	40	32	20	39	32	19
OTHER INDUSTRIES														
Iron	301						Effluent Diverted to Hamilton WTP							
Cyanide		172												
Zinc		30												
TOTAL														
Iron	64335	59216	42725	20594	8244	15422	34500	6548	11682	17833	10330	7100	9125	5256
Zinc		>30		1411	1499		1100	647				118	266	128
Chromium		>47	>82	127	128		89	36			>27			>6
Copper							133	96			>8			
Lead							22	64			31			
Cadmium							0							
Manganese							570	202						
Cyanide	1937	684	749	688	1536	317	1090	104	977	340	260	138	184	65
Reference	a,l	b,m	c	d	d	e	f	g,n	h	e	f,k	e	e	i,j

">" = loading figures were not available for both steel industries.

REFERENCES FOR TABLE 1.

a. OWRC 1964; b. IJC 1969a; c. OWRC 1968a, b; d. Snodgrass 1981; e. Matchette 1986; f. MOE 1985; g. EPS 1979 a, b; h. Novak et al. 1981; i. Eisler 1986; j. Wilson 1986; k. Holmes 1986; l. Other industries include CIL, International Harvester, Stanton Pipes, National Steel Car, Cyanamid, Firestone, Domtar, and Proctor and Gamble; m. Other industries include Firestone, National Steel Car, Stanton Pipes, Canadian Industries, International Harvester and Domtar; n. STELCO hot forming mill effluent sampled in 1979; o. DOFASCO cold finishing mill effluent samples in 1979.

Net industrial iron loadings to Hamilton Harbour have decreased 91.8% between 1964 and 1985 to the current level of 5256 kg/d (Fig. 3). Cyanide loadings have likewise decreased by 96.7% to about 65 kg/d while zinc and chromium loadings decreased by more than 70%. Recent figures for other metals are lacking for comparison.

The increase in some loadings in 1977 appears anomalous. In that year, loadings were calculated using the detection limit as the concentration when levels were below detection (Vogt 1986); this procedure would inflate estimates. However, since iron levels are generally above detection limits, the iron loadings are probably correct and the increase may be related to the level of industrial activity.

2.1.2. Leachate from Industrial Sites

Leachate may enter the south shore of Hamilton Harbour from bayfront industries via storm sewers (Van Biesbrouck 1986). The estimated metal loadings from leachate in 1984 for the steel mill sites (Table 2) are very low relative to direct discharge (Table 1). Comparisons for mercury are not possible since their concentrations in direct discharges were undetectable (Wenzsel 1986).

Table 2. Estimated loadings of metals and cyanide from steel mill site leachate in 1984 (kg/d) (Van Biesbrouck 1986).

Iron	1.311
Cyanide	0.087
Zinc	0.110
Copper	0.021
Lead	0.241
Nickel	0.059
Cadmium	0.019
Chromium	0.060
Arsenic	0.015
Mercury	0.001
Silver	0.039

It is likely that leachate is not generated uniformly on the steel mill sites due to large storage piles of ore and coal. Coal piles are sprayed with water and tallow to minimize dust erosion and the possibility of spontaneous combustion. Leachate is probably reduced in these locations because of high absorption and surface evaporation (Van Biesbrouck 1986). Runoffs from coal, ore and coke breeze piles are a source of metals to the steel mill sites (Table 3) and possibly to their leachate. Since no estimate of runoff volumes are available, and since the measurements are highly variable, no loading estimates can be calculated.

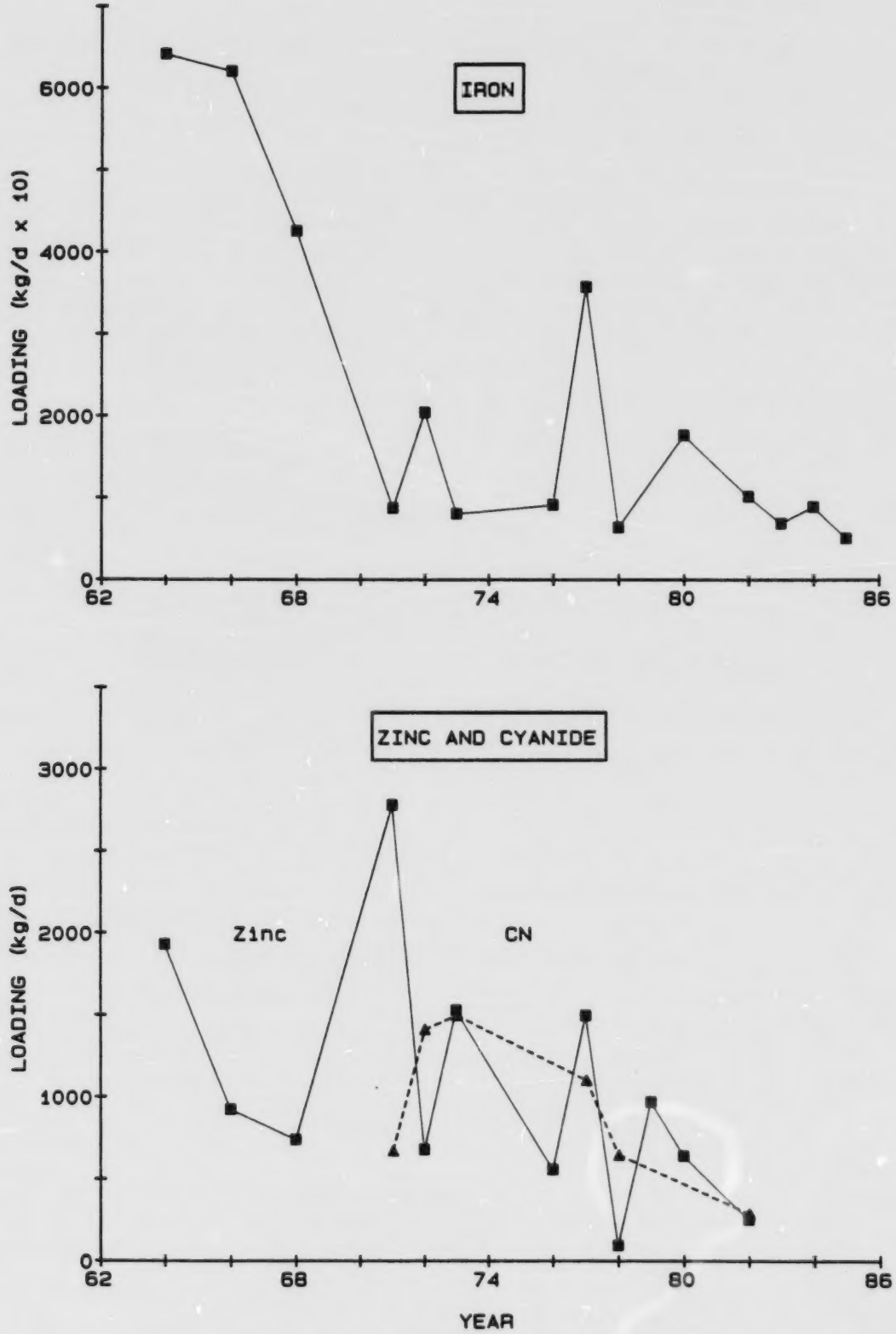

Figure 3. Industrial loadings of iron, zinc and cyanide to Hamilton Harbour. Note that the scale for iron is 10-fold higher than for zinc and cyanide.

Table 3. Chemicals in runoff from raw materials stored by steel industries (mg/L) (EPS 1978a; 1978b; 1979b)

Substance	DOFASCO			STELCO
	Coal Pile	Ore Pile	Coke Breeze (Fines)	Coal Pile
Iron	60.70	3.35	80.60	5.20
Cyanide	0.13	0.21	0.01	0.04
Phenol	0.10	0.11	0.05	0.009
Oil & Grease	14.00	7.00	1.00	12.00

2.1.3. Atmosphere

Industrial atmospheric loadings are primarily dust emissions from stacks and from coal and slag piles. Coal and slag pile emissions were about 0.97 and 0.5 ton/acre/a respectively (Ontario Research Foundation 1982). No chemical analysis of these emissions are available but bituminous coal used in the steel industry contains many trace metals (Table 4). Using zinc as an example, daily loadings would be equivalent to about 0.02 kg/ha/d, a trivial amount relative to aqueous emissions (Table 1) or metals in rainfall (see section 2.5.).

Table 4. Average trace element levels in bituminous coal (U.S. Department of the Interior 1978)

Element	Concentration (mg/kg)	Element	Concentration (mg/kg)
Arsenic	16.0	Manganese	21.0
Barium	70.0	Mercury	0.2
Beryllium	0.8	Molybdenum	9.8
Boron	15.0	Nickel	20.0
Chromium	24.0	Selenium	3.7
Cobalt	18.0	Tin	1.1
Copper	13.0	Vanadium	33.0
Fluorine	90.0	Zinc	22.0
Lead	5.2	Zirconium	68.0
Lithium	64.0		

In the past, an unknown amount of iron ore and coal dusts were swept into the Harbour. Complaints of heavy coal dustfall on Beach Boulevard at the east end of Hamilton Harbour were documented in the winter of 1966 (HML 1966), and again in the mid 1970's (Vogt 1986). After the latter incident, measures were taken to reduce this emission by spraying the pile with water in the summer and with tallow in the winter (Vogt 1986). During extraction for use, the coal is taken from the downwind side of the pile and a snowfence is placed on top to slow the wind velocity. Slag piles are now stored only on the property of National Slag and may be an unmeasured source of metals to Windermere Basin.

While quantitative estimates of total loadings are unavailable, iron in dustfall on the beach strip to the east of the industrial zone indicates the relative importance of these sources (Table 5). Since winds are from the west and southwest 40 to 65% of the time in any given month (Holmes 1986), much of the dust would be blown towards the beach strip and over the Harbour between the industries and the beach (Fig. 1). Iron deposited on the beach from dustfall increased between 1958 and 1975 (Table 5). No analyses of metals in dustfall were available after 1975 but the present contribution is thought to be unchanged (Vogt 1986). If a "worst case" situation were assumed, i.e. the loading on the beach strip applied to the entire harbour, the daily input of iron from the atmosphere would be about 550 kg/d or 20% of the loadings from aqueous discharges (Table 1). The actual amount would probably be much less since only part of the Harbour is downwind at any one time and some of the dustfall on the beach strip will be from traffic on the QEW.

Table 5. Iron in dustfall in the beaches area
(HML 1958; 1962; 1963; 1966; Dobroff 1986)

Year	Annual Dustfall (kg Fe/ha/)
1958	36.78
1962	89.74
1963	73.56
1966	80.91
1973	92.68
1974	82.38
1975	97.09

2.2 WASTEWATER TREATMENT PLANT LOADINGS

2.2.1. Effluent

Iron loadings from WTPs are relatively minor (Table 6), equivalent to 3.5% of the total estimated input to the Harbour in 1986 (see discussion, Section 5.1 Table 31). For other trace metals, however, WTPs are a more significant source. For instance, 11.6% and 18% of the total Harbour inputs of chromium and zinc are from WTPs. Similarly WTPs appear to be major sources of nickel and cadmium but this is partly due to a lack of information on industrial loadings (Table 31).

Table 6. Loadings of metals from wastewater treatment plants (kg/d). (Smart 1975; MOE 1985)

	Hamilton WTP				Burlington WTP		
	1975	1977	1982	1982-83	1975	1982	1983
Iron		299.0	230.0	139.8	7.0	64.0	61.0
Copper	9.5	18.0	9.5	5.55	1.0	2.7	1.7
Nickel	18.0	13.0	13.0	10.9	2.0	<1.0	0.4
Zinc	40.0	86.0	21.0	27.5	5.0	7.0	8.6
Manganese	20.0	33.0	24.0	NA	5.0	3.5	6.8
Cadmium	2.7	1.3	<0.5	0.3	NA	<0.2	0.5
Chromium	18.0	38.0	<9.0	5.5	1.0	1.0	0.4
Lead	8.6	10.1	<7.0	1.9	NA	<2.0	<0.4
N	9	1	12-14	12-14	1	12-14	15

NA = not available

In 1976, the Hamilton WTP removed metals more efficiently (76%) than an average of 11 other Ontario WTPs (48%) with similar treatment (Atkins and Hawley 1978) and recently more than 80% removal efficiency was achieved (Zukovs et al. 1984). However, more than 250 kg/d of all metals still enter the Harbour since these efficiencies apply to very high inputs to the WTP from metal-related industries, including STELCO and DOFASCO (Zukovs et al. 1984). A more recent report suggests that current removal efficiencies for metals at Hamilton's WTP are the same as for other Ontario plants (MOE 1986a).

Recent increases in the levels of iron and copper in the effluent of the Burlington WTP (Table 6) may be the result of the introduction of phosphorus removal by ferric chloride (MOE 1985). The Burlington WTP adds 4.5 mg/L of (Fe_{3+++}) in the tertiary stage for a total of 109,000 kg per year (Wyman 1986). Ferric chloride used in WTPs contains trace amounts of various metals (Table 7), but the exact contribution to loading is unknown. Elevated metal loadings may also be due to the growth of population and industry in Burlington.

Table 7. Trace metals in ferric chloride used for phosphorus removal in wastewater treatment plants (Black 1986).

Metal	Concentration (mg/kg)
Zinc	48.0
Copper	5.0
Nickel	9.4
Lead	<0.60
Cadmium	<0.05
Chromium	6.7
Molybdenum	0.42
Cobalt	15.0
Arsenic	0.2
Aluminum	80.0

The metals from the Dundas and Waterdown WTP effluents are included in loadings from Cootes Paradise and Grindstone Creek (see section 2.3).

2.2.2. Sewage Sludge

Sewage sludge, the solid waste product of sewage treatment, can be buried, applied to land as agricultural fertilizer, or incinerated. Hamilton incinerates its sludge using two multiple hearth incinerators. In pilot scale tests, Hamilton sludge was incinerated at the Hamilton WTP and the fate of metals tested (Campbell et al. 1982). Zinc, iron, magnesium, aluminum, nickel, copper, chromium, and silica remained in the ash and were buried in landfill (Zukovs et al. 1984). Some cadmium, mercury, and arsenic were found in the gas stream and might enter the Harbour via the atmosphere. However, the overall contribution to loadings would likely be quite small, based on the rough estimates in section 2.1.3 (Atmosphere).

Burlington's sewage sludge was traditionally applied to land in the Halton region and did not enter Hamilton Harbour directly. In studies of sludges typically used for land application in southern Ontario, Burlington's exceeded the guideline for maximum loadings to Ontario soils for cadmium (Webber et al. 1983). The sludge from the Burlington Skyway WTP is now incinerated at the Hamilton WTP to solve this problem.

2.3 STORM SEWER AND TRIBUTARY LOADINGS

Except for cadmium, Hamilton storm water is a greater contributor of metals to the Harbour than Burlington stormwater (Table 8) but, overall, stormwater is a very minor source compared to industrial discharges (Table 31). These loadings, of course, do not consider storm water from the escarpment which is included in tributary loadings from Cootes Paradise and Redhill Creek.

Table 8. Estimated loadings of metal and cyanide from storm sewers (kg/d) (Snodgrass 1981; MOE 1985)

	Hamilton	Burlington
Iron	80.0	9.0
Zinc	8.8	1.0
Copper	0.7	0.6
Lead	1.5	1.2
Nickel	0.2	
Cadmium	0.1	0.2
Manganese	8.3	2.0
Chromium	1.1	0.8
Arsenic	0.04	
Cyanide	1.0	0.0

Metal loadings from the major tributaries are quite significant (Table 9) relative to current steel plant emissions (Table 31) but loading data more recent than 1979 were not available. However, measurements of the levels of metals in these waters have not changed significantly since 1979 (MOE 1986c). Therefore, assuming that total annual flow is similar to 1977, 1986 loadings should be similar (Vogt 1986). It is possible that iron loadings from Cootes Paradise represent increased amounts of suspended soil rather than industrial emissions. There are high concentrations of suspended solids in Cootes due to resuspension of mud and to soil erosion.

Table 9. Loadings of metals and cyanide from major tributaries (kg/d). (MOE 1985; Snodgrass 1981; Novak *et al*. 1981; Holmes 1986)

1977	Cootes Paradise	Redhill Creek	Grindstone Creek	Total
Iron	1100	18	12.4	1130.4
Zinc	23	1.7	1.7	26.4
Copper	7.6	0.83	0.83	9.3
Lead	10	2.5	2.5	15.0
Cadmium	1.8	0.42	0.41	2.6
Manganese	88	8.0	8.0	104.0
Chromium	7	1.7	1.7	10.4
Cyanide	0	0	0	0
1979				
Iron	680	18		>698
Flow (1000 m^3/d)	345			>345

2.4 NON-POINT SOURCE LOADINGS

The input of metals and cyanide from shipping and spills is unknown, although acid, alkali and plating solutions are occasionally spilled directly into the Harbour (see section 3.4.2, Table 20).

2.4.1. Atmosphere

Metal loadings from Hamilton rainfall for 1970-71 were estimated by Shiomi and Kuntz (1973). The loadings ranged from 0.1 kg/d for cadmium to 6.1 kg/d for zinc. Loadings of metals in precipitation to the Harbour have decreased and are now 0.03 kg/d or less for these metals (Chan 1986); these values are similar to rough estimates of zinc loading in coal dust (section 2.1.3). However, the sample locations and research techniques were different for each study and the influence of these factors is unknown. Atmospheric sources to the Harbour appear to be very minor contributors of metals.

Automotive emissions of lead, vanadium and cadmium could enter the Harbour through the air or via runoff from roads. It is estimated that 3/4 of the lead in gasoline is emitted in automotive exhaust (Vena 1986). Currently the concentration of lead in Canadian gasoline is 0.28 g/L so an emission rate of 0.21 g/L of lead from cars using this gasoline is expected (EPS 1985). Pollutants that do not disperse from the Skyway Bridge might eventually enter Hamilton Harbour since bridge runoff is directed to the land beneath the bridge. The concentrations of chromium and lead in leachate from excavated soil under the Skyway Bridge exceed MOE leachate quality criteria (Table 10). Runoff from other automotive routes in the Hamilton Harbour area is accounted for in storm water (section 2.3).

Table 10. Chemical concentrations in leachate from subsoil materials sampled from the site of the QEW widening (Nov. 8, 1985; Foster 1986).

Parameter (mg/L)	Sample Number 1.	2.	3.	4.	5.	Regulation 309 Leachate Quality Criteria
Chromium	0.09	0.1	0.1	0.1	0.07	0.05
Cyanide (total)	<0.01	<0.01	<0.01	0.01	0.01	0.2[a]
Lead	0.56	0.64	0.64	0.12	0.45	0.05
PCBs	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	0.003

[a] Leachate quality criterion for free cyanide

2.4.2. Landfill Leachate

A study of Burlington's Bayview Park landfill concluded that inorganic chemicals in groundwater are rarely observed anywhere but very close to the landfill site (Barker et al. 1984); however, groundwater inputs to the Harbour have yet to be studied. Surface water runoff from that same site does contribute heavy metals to Indian Creek: on March 26, 1986, 12.5 mg of iron per minute entered Indian Creek; by June, input fell to 5 mg/min (Benson 1986). This will be included in stormwater runoff.

2.5 LEVELS

2.5.1. Water

Measurement of metal concentrations in water on a harbour-wide scale began in 1980. Limited data for iron and zinc in water are also available from 1964 and 1975. However, the earlier zinc data are suspect and have been omitted because of an unexplained two-fold increase in concentration between 1979 and 1980 (MOE 1986b).

In general, metal concentrations declined between 1980 and 1984 for all areas (Table 11). The Harbour's south shore waters were often the most contaminated for the majority of metals (e.g. iron, Figure 4a) although Windermere Basin had the highest concentrations of lead, copper, nickel, and zinc in 1982 and 1984 (e.g. copper, zinc, Figure 4b) assuming the 1982 Windermere Basin data are comparable to 1984 Harbour data. Recent concentrations are generally less than the objectives established by the IJC, with the exception of copper, lead and zinc.

Levels of cyanide in water were measured between 1980 and 1982. Early values were about double the water quality objective for cyanide but later values were less than the detection limit, which corresponded to the objective of 5 µg/l (Table 11).

2.5.2. Sediments

Sediment metal levels were available for 1975, 1980 and 1985 and iron levels were also reported in 1964 (Table 12). In 1980 the top 3 to 5 cm were sampled and in other years the top 3 cm. No indication of the amount of sediment sampled by Hamilton Municipal Laboratories (HML 1964) was given. In the absence of sampling information, we assumed the data to be equivalent.

Sediment metal concentrations increased over time in the Harbour as shown by a sediment core taken from the central basin (Fig. 5). When sectioned, analysis of layers indicated that metal levels began to rise around 1890, corresponding to the establishment of iron foundries in Hamilton (Nriagu et al. 1983). Levels decreased from 1964 to 1975 (Fig. 5), and more recent sampling has indicated that levels of all metals increased again between 1975 and 1985 (Fig. 6).

Table 11. Geometric mean levels of metals in water (µg/L) (calculated from MOE 1986b; IJC 1977; 1978; 1980))

Year	Area[1]	N	As	Limits[2]	Cu	Limits	Cd	Limits	Cr	Limits	Pb	Limits	Hg	Limits	Ni	Limits	Mn	Limits	Zn	Limits	Available CN	Limits
1980	SS	4			16	1-26	<3	1- 7	11	6-20	22				25	20-32	94	85-103	66	50-80	13(14)	11-16
	EE	2			25		<1		5		30				28		57		42		10	
	NS	2			16		<1		5		12				8		49		32			
	WE	2			16		<2		5		16				16		68		45		10	
	CB	2			15		<2		5		11				6		58		37		10	
1981	SS	1			14		.2		9		11		0.226		14		80		40		6(4)	5.9-6.1
	EE	1			13		.2		3		9		0.230		8		38		18			
	NS	0																				
	WE	1			13		.2		3		9		0.170		8		37		7			
	CB	2			14		.1		4		9				9		40		20		<5	
1982	SS	6	1(12)[3]	0.99-1.1	5	4-7	.2	0.1-0.2			6	5-7	0.075(12)	.045-.123	6	5-8	59		29	26-30	<5	
	EE	6			7	6-9	.2	0.1-0.2			4	3-5	0.072(12)	.059-.087	5	4-6	41		17	10-30	<5	
	NS	0																				
	WE	6	1(18)	0.99-1.1	6	5-8	.2				4		0.066(18)	.056-.077	4	3-5	45		16.6	13-20	<5	
	CB	12	1(29)	0.99-1.1	6	5-8	.2	0.1-0.2			6	5-7	0.077(18)	.065-.091	5	5-5.3	56		18	16-20	<5	
	WB	6	1.3(11)	1.2-1.4	12	10-14	.3	0.2-0.3			8	5-10	0.071(19)	.065-.078	17	10-20	87		38	30-50	<5	
1983	WB[3]	17			17		.3				9				30				27			
1984	SS	1	1(2)		9		.2				6		0.075(2)		11		74		30			
	EE																					
	NS																					
	WE	1			1		.3		3		3		0.021		5		59		21			
	CB	2			1		.3				4				6		68		50			
IJC Objective (µg/L)			50		5		.2		50		5		0.200		25				30		5	

[1]SS = South Shore; EE = East end; NS = North Shore; WE = West end; CB = Central Basin; WB = Windermere Basin.

[2]Limits - 95% confidence limits for sample sizes greater than 2.

[3]Value in brackets after the mean is the number of samples the mean is based on if other than that already stated.

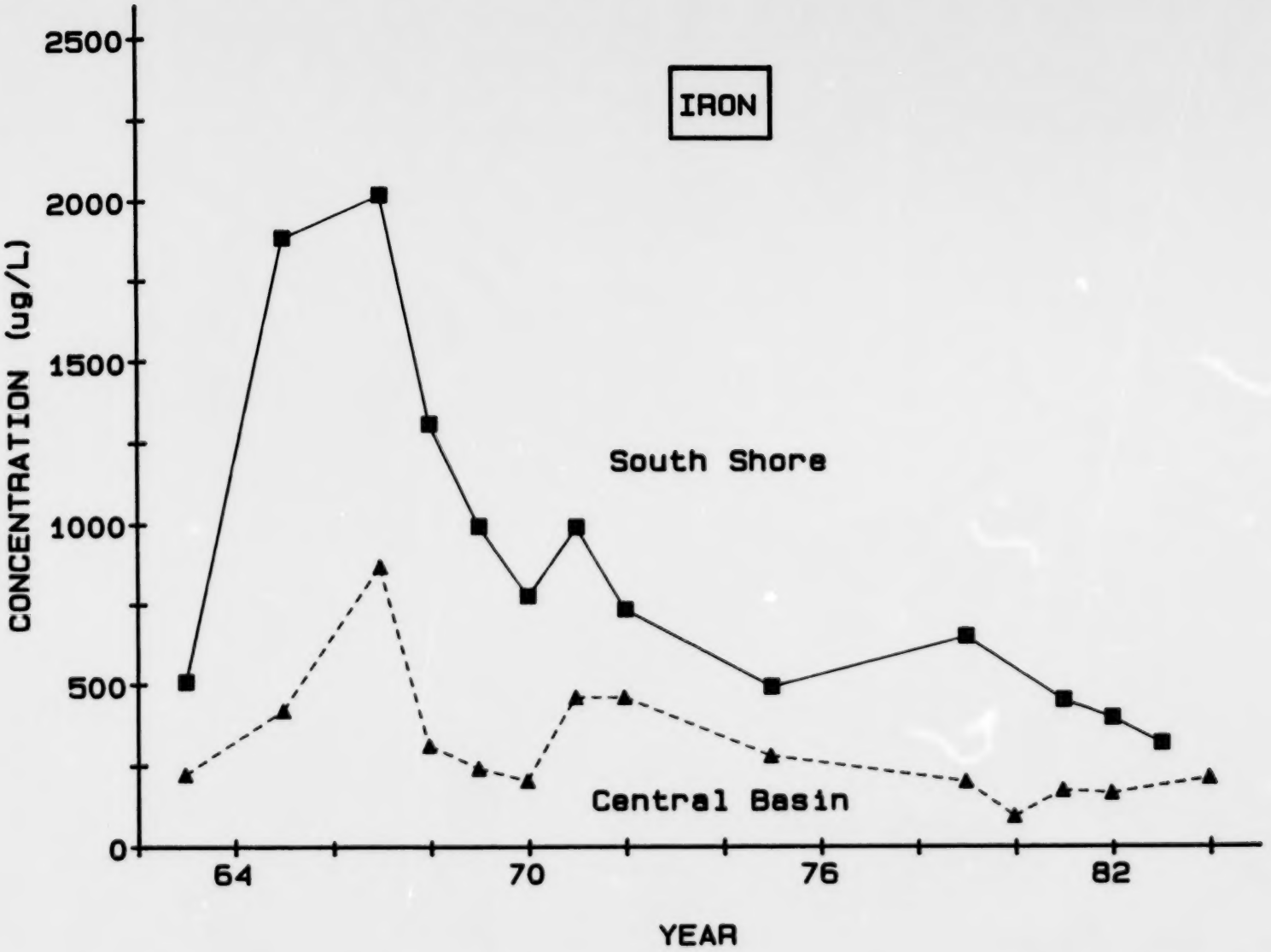

Figure 4a. Concentrations of iron in Hamilton Harbour, 1964 to 1982.

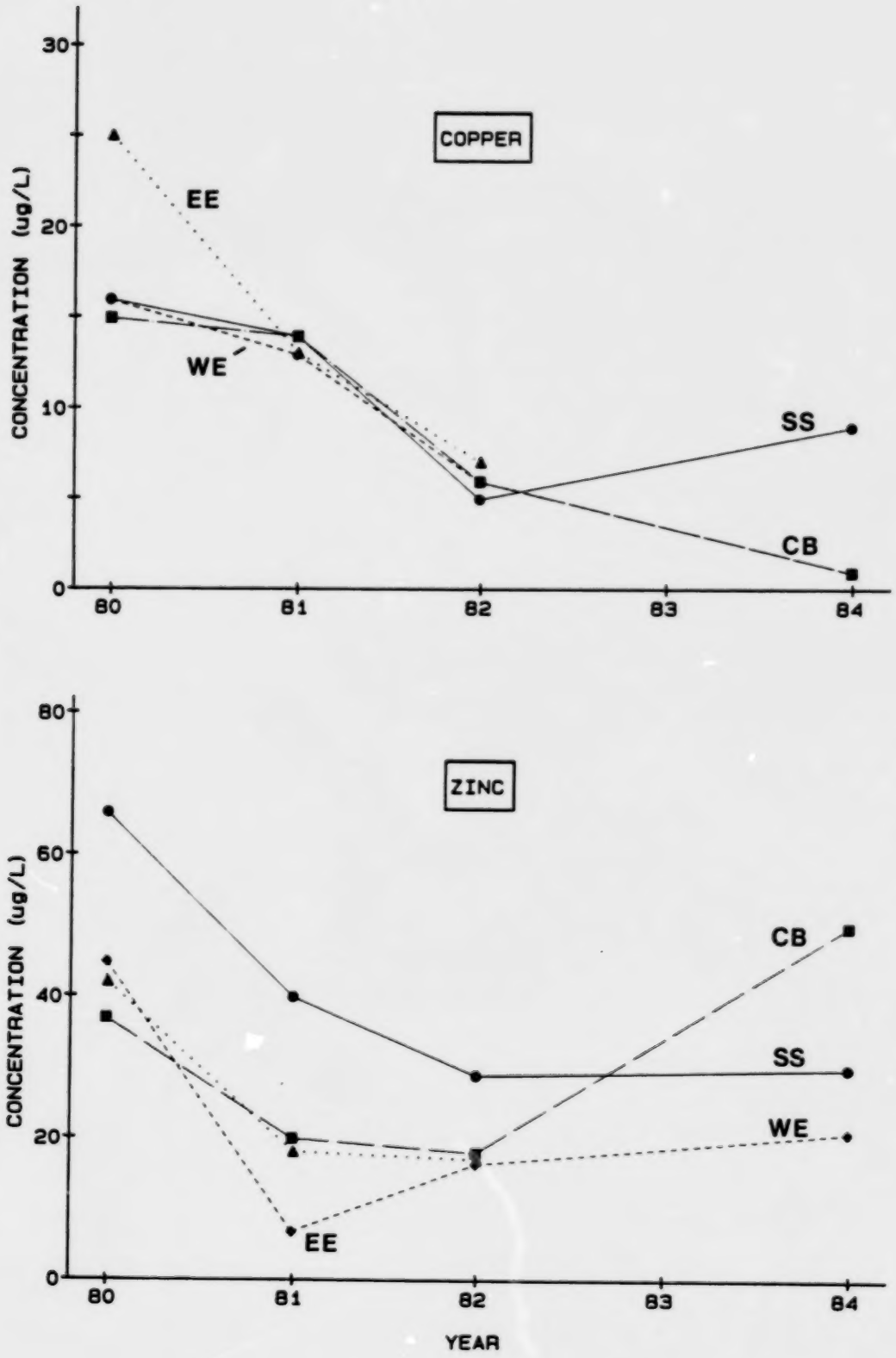

Figure 4b. Concentrations of copper and zinc in Hamilton Harbour 1980 to 1984. The zones indicated are: SS = South Shore; CB = Central Basin; WE = West End; EE = East End.

Table 12. Geometric mean levels of metals in sediments (ug/kg dry weight). (MML 1964; MOE 1977; MOE 1986b; Cairns 1985)

Year	Area	N	Fe[1]	Limits[2]	Hg	Limits	Cd	Limits	Cr	Limits	Pb	Limits	Zn	Limits	Ni	Limits	Co	Limits	As	Limits	Cu	Limits	V	Limits
1964	SS[3]	14	125																					
	EE	2	91																					
	NS	6	41																					
	WE	5	85																					
	CB	15	87																					
	WB	2	52																					
	LO	25	38																					
1975	SS	34	59	50-69	0.35	0.29-0.41	2.9	2.5-3.4	128	89-184	194	124-303	1520	1014-2270	30	26-34								
	EE	6	15	14-17	0.02	0.01-0.02	0.5	0.31-0.67	18	16-21	8	5-14	95	67-134	10	9-12								
	NS	6	25	21-30	0.13	0.09-0.18	2.3	1.4-3.8	42	28-64	62	42-91	619	405-947	20	16-26								
	WE	9	38	34-43	0.31	0.25-0.38	3.9	0.3-4.6	54	45-65	101	84-121	667	530-840	32	29-35								
	CB	19	54	37-76	0.40	0.33-0.47	4.3	3.7-5.0	84	71-99	150	127-176	1111	923-1323	31	28-34								
	WB	3	7	3-18	0.26	0.11-0.57	4.8	2.1-10.0	172	86-343	175	82-376	869	428-1765	51	42-62					136	11-17		
1980	SS	6	96	73-126	0.21	0.15-0.28	4.4	3.5-5.5	212	153-292	430	298-622	2642	1928-3620	46	40-53	10	9-11			35			
	EE	1	23				3.1		51		61		840		22		4				84			
	NS	2	49		0.27		5.7		140		200		2500		39		8				94			
	WE	3	40	26-61	0.14	0.06-0.32	5.3	2.7-10.	82	37-184	185	96-355	1871	440-7946	46	35-61	12	10-14			99	62-160		
	CB	6	50	31-79	0.18	0.03-0.9	3.1	1.0-9.7	134	31-571	178	78-408	1823	250-13294	36	13-101	9	6-13			340			
	WB	1	41		0.48		7.6		710		460		2400		67		14							
1985	SS	16	104	89-121					216	186-250	208	177-245	1738	1459-2072	38	34-43	12	11-14	13	11-15	86	75-99	50	45-54
	EE	2	80						67		94		745		33		13		5		47		53	
	NS	5	86	58-129					240	193-298	306	257-364	3217	2539-4076	54	51-57	19	17-20	23	18-29	102	86-120	71	55-91
	WE	5	54	43-68					105	73-151	172	121-245	1457	845-2510	43	29-64	19	16-24	13	8-20	79	37-16	61	37-100
	CB	17	83	71-96					420	268-657	524	326-844	3239	2809-3737	49	45-54	20	19-20	25	22-28	113	101-127	74	68-79
	WB	2	43						228		187		693		51		21		5		122		69	
MOE Guideline			10		0.3		1		25		50		100						8		25			

[1] ug/kg dry weight

[2] 95% confidence limits

[3] SS = South Shore; EE = East End; NS = North Shore; WE = West End; CB = Central Basin; WB = Windermere Basin; LO = Lake Ontario

The area of greatest sediment metal contamination depends on the metal studied. Iron levels were consistently higher in south shore sediments than in any other area in the harbour. The central basin ranked second in 1964 and 1975 but in 1980 and 1985 the north shore was equally contaminated (Fig. 6). For zinc the south shore was most contaminated in 1975 but the north shore and central basin are the areas with highest current levels (Fig. 6). Currently, nickel concentrations in sediment are also highest in the north shore area (Fig. 6). The guidelines that limit open water disposal of dredged materials are exceeded for all metals for which a guideline was established (Table 12).

The distribution of sediment metals in the Harbour may be a function of sources, dredging, particulate settling, or erosion. Dredging could be a major factor in the south shore area near Hamilton's industries, since shipping requires deep channels. The result may be lower than expected levels of sediment metals, due to removal by dredging. Disturbance of sediments by propellor action may also prevent the settling of metals complexed by particulates such as algae. In contrast, the deep central part of the Harbour should remain relatively undisturbed; this is a zone with fine silt and clay indicating particulate deposition (Portt et al. 1988).

The high levels of metals in north shore sediments are not associated with any local industrial sources. Instead, they may represent soil erosion or currents that carry metals from wastewater treatment plants.

2.5.3. Biota

For most biota of Hamilton Harbour, metal levels have not been sufficiently studied to establish time trends (Table 13). In particular there are few data on algae, benthos and birds. Limited mercury analyses of fish from 1974 to 1980 show declines in levels in carp (Cyprinus carpio), white perch (Morone americana), yellow perch (Perca flavescens) and alewife (Alosa pseudoharengus) (Table 14). None of the values exceeds MOE's guidelines for consumption of sport fish of 0.5 mg Hg/kg. These species were the only ones sampled more than once and there were few data on other metals in edible portions.

A synoptic survey in 1980 of lead in the blood of fish in Hamilton Harbour demonstrated that carp, white sucker and white perch had levels of 127, 79 and 51 µg/L respectively (Table 13). While not as low as levels in some lake trout from Lake Ontario (9-92 µg/L), they were lower than in carp and suckers from other Lake Ontario harbours (up to 250 µg/L) (Hodson et al. 1983).

Levels of metals in filamentous algae on the surface of Harbour sediments were quite high (Table 13). Relative to the sediments they were associated with, nickel, copper and chromium concentrations were higher while cobalt, zinc and lead were lower. However, the values were close enough that the algae provided a very good estimate of sediment metal. Whether algae took up metal from the sediment or sediments were mixed with the algae was not clear.

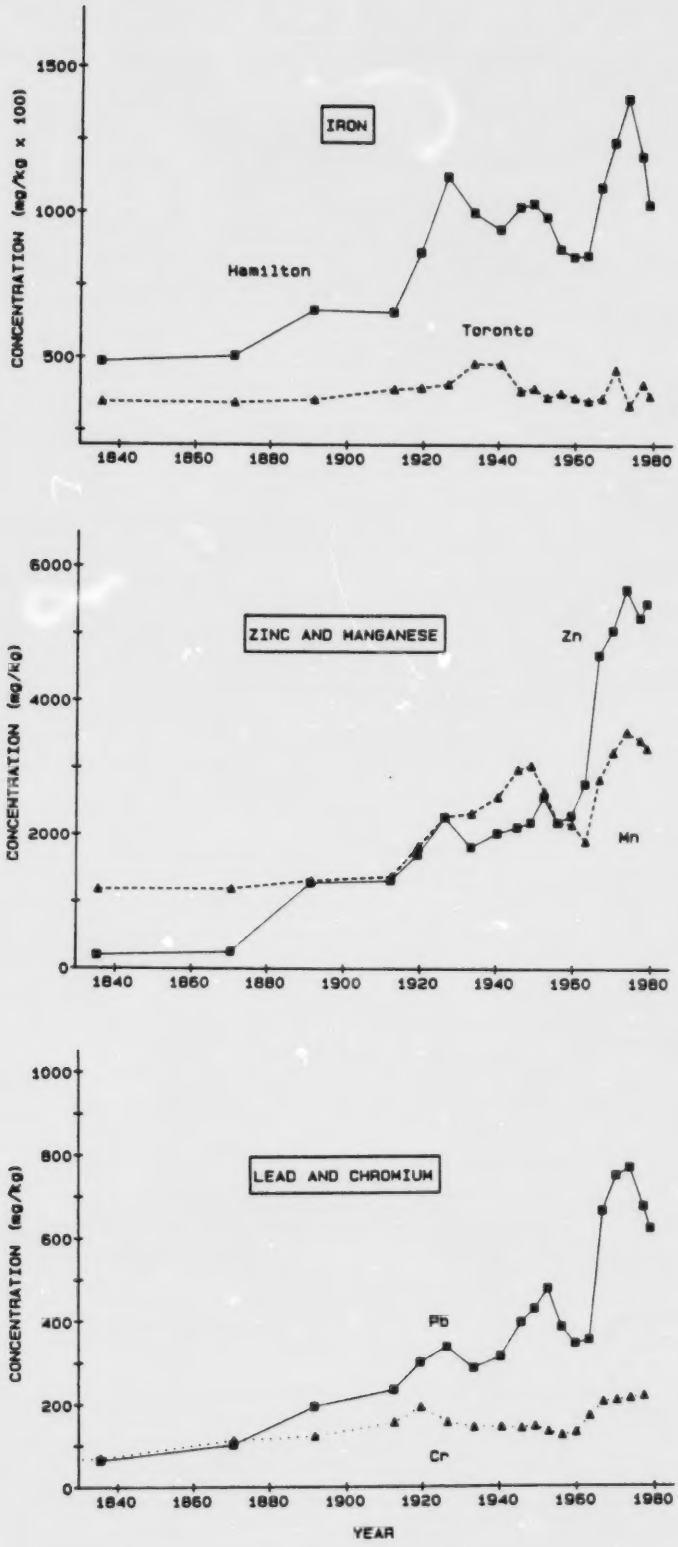

Figure 5. Sediment metal concentrations since 1800, as indicated by dated sediment cores (from Nriagu et al. 1983). Note that the scale for iron concentrations is 100-fold higher than for other metals. The data for Toronto indicate the relative differences in contamination.

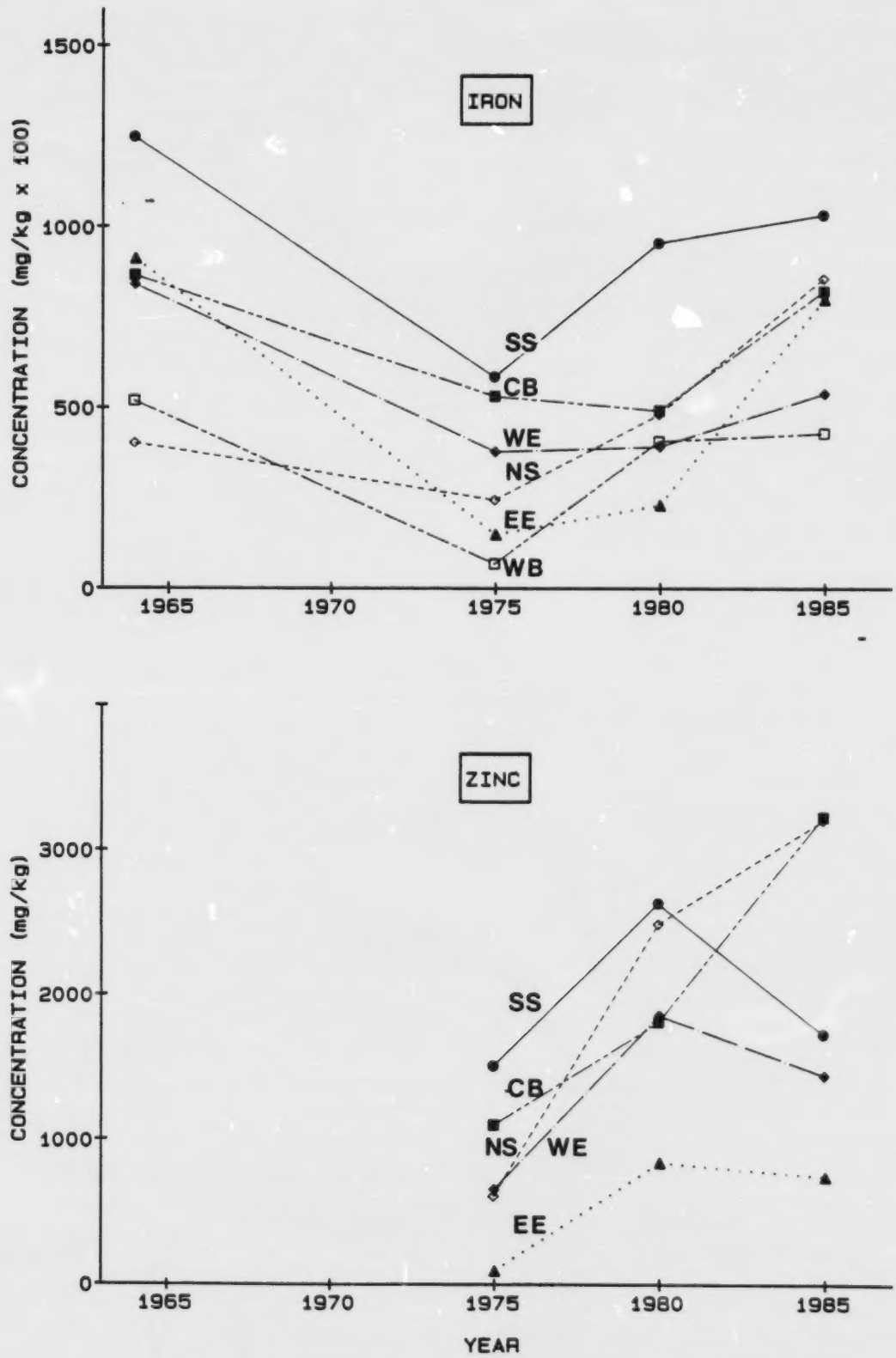

Figure 6. Metal concentrations in sediments since 1965, as indicated by surface dredge samples. Note that the scale for iron concentrations is 100-fold higher than for other metals. The zones indicated are: SS = South Shore; CB = Central Basin; WE = West End; EE = East End; NS = North Shore; WB = Windermere Basin.

Table 13. Metal concentrations in biota.

Organism	Date	Metal	Tissue	N	Geometric Mean Concentration		Reference
Microcystis sp. (algae)	1978	chromium	whole	5	230 (µg/g dry wt.)		Mudroch and Sandilands 1980
		cobalt			16.9		
		copper			166		
		lead			211		
		nickel			107		
		zinc			1690		
Carp (Cyprinus carpio)	1980	lead	blood	152	127 (114-140)[1](µg/L)		Hodson et al. 1983
White sucker (Catostomus commersoni)	1980	lead	blood	84	79 (65-97)[1]		
White perch (Roccus americana)	1980	lead	blood	166	51 (43-60)[1]		
Herring gulls (Larus argentatus)					Adult (µg/g wet weight)	Fledgling	
	1983	cadmium	liver	9	0.342	0.022	Struger et al. 1987
			kidney		2.16	0.033	
			feather		0.104	0.062	
			bone		0.006	0.006	
		lead	liver	9	0.13	0.06	
			kidney		6.9	0.12	
			feather		7.9	0.93	
			bone		15.0	0.56	
		mercury	liver	9	0.342	0.022	
			kidney		2.16	0.033	
			feather		0.104	0.062	
			bone		0.006	0.006	

[1] 95% confidence limits

Table 14. Arithmetic mean concentrations of metals in fish muscle (fillets) (MOE 1986d; Cairns 1986)

Year	Species	N	Length (cm)	Weight (g)	Metal (mg/kg wet weight) Hg	Cu	Ni	Zn	Pb	Cd	Mn	Cr	As	Fe	Al	Se
1976	Red horse Sucker	5	36.3	607	0.12	0.95	<.57	7.10	<.38	<.09	0.23		0.07			
	Carp	2	56.5	2518	0.06	0.55	<.49	18.50	<.33	<.08	0.36		0.06			
	Rainbow Smelt	2	20.3		0.24	1.40	<.74	28.50	<.5	<.13	1.90		0.38			
	Alewife	2	15.2		0.14	1.40	<.59	25.00	<.4	<.09	1.12		0.51			
	Yellow Perch	2	22.9	142	0.26	0.63	<.79	8.10	<.53	<.13	0.48		0.03			
	White Perch	2	16.5	85	0.06	2.05	<.53	7.95	<.35	<.09	0.45		0.04			
	Rainbow Smelt	19	18.8	43	0.19											
	Coho Salmon	4	51.5		0.16											
1979	Lake Trout	1	51	1500	0.37											
	Coho Salmon	5	54	1650	0.10											
1981	Alewife	5	14	18	0.03											
	White Perch	8	17.3	66	0.05											
	Yellow Perch	2	12	20	0.03											
	Black Bullhead	2	28	290	0.10											
	Pumpkinseed	1	13	50	0.04											
	Black Crappie	1	22	150	0.03											
	Carp	7	52.6	1936	0.04											
	Pike	9	65.2	1433	0.32											
	White Sucker[1]	10	42.2	885		1.07	0.02	15.18	0.17	0.045		<.02	0.12	24.76	5.1	0.42

[1] Whole fish

Gulls were also highly contaminated (Table 13), containing more mercury in liver and kidney, more lead in feathers and kidney, and more cadmium in all tissues than in gulls from other locations (Lakes Erie, Huron and Superior).

3.0 ORGANIC CHEMICALS IN HAMILTON HARBOUR

3.1 INDUSTRIAL LOADINGS

Steel mills are known sources of many organic chemicals, chiefly phenols, polynuclear aromatic hydrocarbons (PAHs) and oil and grease. Records of the discharge of phenols and oil and grease from the steel mills have been kept since 1964, but PAHs were first measured in the 1970s.

From about 1965 to 1978, a Westinghouse plant in Hamilton made electrical transformers that required Arochlor 1254 and 1260 (polychlorinated biphenyls, PCBs) as thermostable dielectric fluids. This plant was located above the Strathearne sewer but records of amounts used or discharged are not available (Duffus 1986). Continuous PCB emissions from the steel mills are unlikely since MOE has not found PCBs in steel company effluents (Vogt 1986), but periodic spills from electrical equipment may occur.

Since the analysis of organic chemicals is a relatively recent part of monitoring programs, there is little data on other major industrial groups. For example, the textile industry may have discharged organic dyes before the mid-1950's when these industries failed.

3.1.1. Direct Discharge

Large quantities of phenolics are produced by the steel industry; loadings to the Harbour peaked in 1972 (Table 15) and have decreased 96% since then (Fig. 7). Many other trace organic chemicals are found in steel mill effluents (Table 16) but are treated before discharge. The bulk of these compounds are formed in the coking process and include known carcinogens and mutagens (Hallett and Brecher 1984). The proportion removed during treatment is unknown, but the 1986 estimated total loading of PAHs to the Harbour from industrial direct discharge is 1.75 kg/d or 0.64 tonnes/a (Vogt 1986); no previous loading value was available for comparison. Emissions from the steel industry represent the largest source of benzo(a)pyrene (BaP) in Ontario, followed by forest fires (Statistics Canada 1978).

3.1.2. Leachate from Industrial Sites

Leachate from a steel mill site sampled in 1984 was estimated to carry about 1.8 kg/d of phenols to Hamilton Harbour (Van Biesbrouck 1986), or about 5.0% of the total current phenol loadings. No other organic chemicals were sampled but PCBs, PAHs, oil and grease and other organic chemicals may also enter Hamilton Harbour by this route (Van Biesbrouck 1986). Oil, grease and

Table 15. Loadings of phenols and oil and grease from industries in Hamilton (kg/d).

Substance	Year	1964	1966	1968	1972	1973	1976	1977	1978	1979	1980	1982	1983	1984	1985
STELCO															
phenol		476	698	467	6	240		170	29	102	172	260	64	43	31
oil and grease		1257	18403	58060	4990	3357	2722		9999	2148	2596		1370	3244	2167
DOFASCO															
phenol		254	149	172	1860	473		25	12	48	91	48	16	15	3
oil and grease		1660	11406	7256	5239	3251	2722	28	867	107	635		207	464	429
OTHER INDUSTRIES															
phenol		4	8	- - - - - - - - - Effluent Diverted to Hamilton WTP - - - - - - - - - - - - - - - -											
oil and grease		255	149				"	"		"	"				
TOTAL															
phenol		734	855	639	1866	713		195	41	150	263	308	80	58	34
oil and grease		3172	29809	65316	10229	6608	5444	28	10866	2255	3231		1577	3708	2596
References:		a,l	b,m	c	d	d	e	f	g,n	h	e	f,k	e	e	i,j

a. OWRC 1964; b. IJC 1969a; c. OWRC 1968a,b; d. Snodgrass 1981; e. Matchette 1986; f. MOE 1985; g. EPS 1979; h. Novak *et al.* 1981; i. Eisler 1986; j. Wilson 1986; k. Holmes 1986; l. Other industries include CIL, International Harvester, Stanton Pipes, National Steel Car, Cyanamid, Firestone, Domtar, and Proctor and Gamble; m. Other industries include Firestone, National Steel Car, Stanton Pipes, Canadian Industries, International Harvester and Domtar; n. STELCO hot forming mill effluent sampled in 1979; o. DOFASCO cold finishing mill effluent samples in 1979.

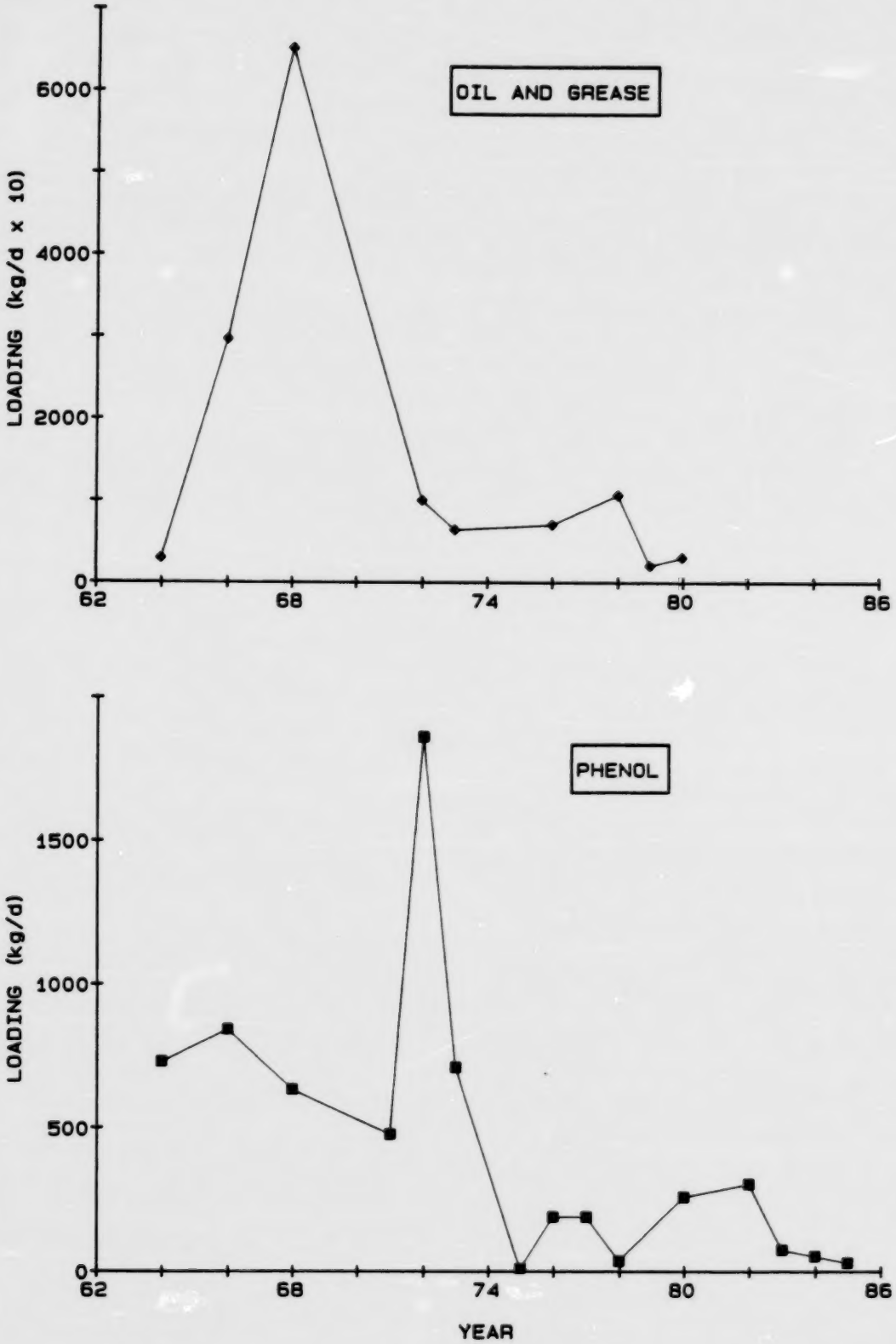

Figure 7. Industrial loadings of oil and grease and phenols to Hamilton Harbour. Note that the scale for oil and grease is 10-fold higher than for phenols.

Table 16. Organic chemicals (µg/L) in steel mill wastewater samples before treatment (EPS 1984)

Compound	Coke Plant Waste[2] Jan. 7/82	Blast Furnace Water Jan. 20/82	Blast Furnace Water Jan. 20/82	Coke Plant Waste[3] July 6/82	Combined Waste Apr. 2/82
BASE NEUTRAL GROUP					
Polynuclear Aromatics					
Benzo(A)anthracene and/or Chrysene				160	
Benzo(b) and/or Benzo(k) fluoranthene				410	
Benzo(a)pyrene				240	
Fluoranthene				70	
Napthalene		<10	<10	10	
Pyrene				50	
Chlorinated Benzenes					
1,3- and/or 1,4 Dichlorobenzene		10	20		20
Nitrosamines					
N-nitrosodiphenylamine					130
Phthalate Esters					
Di-n-butylphthalate	ND/50	<10	20		3440
Di-n-octylphthalate					580
Bis(2-ethylhexyl)phthalate		<10			
ACID GROUP					
2-chlorophenol			<10		
2,4-Dimethylphenol		<10			
Phenol	53,000/21,200				
NON-PRIORITY POLLUTANTS					
Aniline	600/920				
Isoquinoline		<10	<10		240
2-methyl naphthalene	ND/40	<10	<10		
Indole	3,000/2,700				1000
Carbazole		<10	<10		
2 or 8 methyl quinoline	ND/200		<10		
Benzothiazole		<10			
Quinoline	6,000/7,500	10	20		1240
1-methyl naphthalene	ND/50		<10		140
4-methyl quinoline			<10		
7,8-benzoquinoline					30
9-anthracene carbonitrile					30

FOOTNOTES:

ND = Not Detected

1 Detection limits of 10 µg/L for baseneutral group, 25 µg/L for acid group except dinitrophenol and dinitrocresol (250 µg/L) unless noted.

2 Analysed in duplicate. Detection limit of 2300 µg/L for base-neutral group, 600 µg/L for acid group.

3 Analysed for PAH's only. Detection limit of 10 µg/L.

The following chemicals were not detected:

Acenaphthene
Acenaphthylene
Anthracene
Phenanthrene
Benzo(ghi)perylene
Fluorene
Bichlorobenzene
Hexachlorobenzene
Butyl benzylphthalate
Diethylphthalate
Dimethylphthalate
Hexachlorobutadiene
2,4,6-trichlorophenol
Pentachlorophenol
2,4-dimethyl pyridine
3,4-dimethyl pyridine
7A-methyl quinoline
2,6-dimethyl pyridine
Quinoxaline
3,5-dimethyl pyridine
Dibenzofuran
Bis(2-chloroethyl)ether
2,4-dimethyl quinoline
7B-methyl quinoline
2,6 and/or 2,7 dimethyl quinoline
3,4 and/or 5,6 benzoquinoline

phenols are components of runoff from coal, and/or coke-breeze piles (Table 3). Although no analyses have been performed, they are also suspected sources of PAH. The use of waste tallow on coal piles in the winter to curtail dust erosion may be one source of "oil and grease", but tallow could decrease the loadings of other chemicals to the Harbour by decreasing wind erosion of the coal.

Leachate from the Westinghouse transformer plant site may have also entered the Strathearne Slip and the south shore zone, an area heavily contaminated with PCBs (MOE 1985; 1986e; also see section 3.6, levels in water and sediment). Since levels in water in the Strathearne Street slip are usually 0.46 - 5.3 µg/L, and occasionally as high as 180 µg/L (MOE 1986e), PCBs may still be leaching from the old Westinghouse site, from its sewers, or from contaminated bottom sediments in the slip. On the north shore in Burlington, the Ontario Hydro transformer station may have contributed PCBs through spills on soil that generated leachate. Current practice at the site is to excavate any stone and gravel on which more than 50 mg/kg PCB was spilled and store it in drums. There are about 350 drums of this type on the site (DellaRossa 1986).

3.1.3. Atmosphere

Past losses of coal and its associated organics to Hamilton Harbour from wind erosion of stored materials were likely greater than present loadings since measures are now taken to reduce erosion (see section 2.1.2). No analyses of industrial stack gases for organic chemicals were found.

3.2 WASTEWATER TREATMENT PLANT LOADINGS

3.2.1. Plant Effluent

Table 17 presents the estimated loadings of chlorinated organic chemicals to Hamilton Harbour through WTP effluents from Hamilton and Burlington; Dundas and Waterdown effluents are included in tributary loadings (section 3.3). The Hamilton plant has an average three- to four-fold higher loading for all chemicals listed, due to its four-fold greater flow (Craig et al. 1984). Loading figures previous to 1982 were available only for PCBs; compared to current levels, these suggest a definite decrease in loading with time. Pesticide loadings are small, ranging from less than the detection limits to 1.9 kg/a for Hamilton and less than detection limits to 1.1 kg/a for Burlington.

The chemicals listed in Table 17 are those that are analyzed routinely, and do not represent a complete inventory. In a study of WTP effluents in 1982, 38 other organic chemicals were found in single 24-hr composites from Burlington and 32 in composites from Hamilton (Table 18; Craig et al. 1984). The plants do not differ significantly in the number of USEPA priority pollutants in their effluent: 14 for Hamilton and 12 for Burlington. Hamilton has a greater concentration of these priority pollutants in seven cases,

Table 17. Loadings of organic chemicals from wastewater treatment plants (kg/a). (Shannon et al. 1976; MOE 1985)

	Hamilton		Burlington	
	1974	1982-83	1974	1982-83
SUBSTANCE				
Total PCBs	25.8	4.6	<1.3	0.9
α-BHC		0.5		0.1
β-BHC		0.4		0.1
γ-BHC		1.8		0.4
α-Chlordane		<0.2		<0.1
γ-Chlordane		0.3		<0.1
Mirex		1.9		0.6
Total DDT		<1.5		<0.1
HCB		1.4		1.1
Dieldrin				<0.1
Total organochlorine compounds	>25.8	10.9		3.2

Burlington in one. The compounds are generally of low molecular weight and include chlorinated compounds, substituted benzenes and phenols, PAHs, phthalates, furans, nitriles, steroids, amides and imidazoles. These single samples may not be representative of the amounts and types of organic chemicals discharged on an annual basis, but they do illustrate their number and diversity.

Zukovs et al. (1984) studied the efficiency of removal of selected organic chemicals in the Hamilton plant in 1982. There was efficient removal of PAHs (>97%) and PCBs (90%) but poor removal of lindane (70%) and pentachlorophenol (63%). No similar data were available for the Burlington WTP.

3.2.2. Sewage Sludge

At the Hamilton WTP, sludge is incinerated and organic chemicals are emitted in the stack gas; atmospheric loadings of PCBs, for example, are 0.96 kg/a (EPS 1983). For PAHs, the Hamilton incinerator has a destruction efficiency (DE) ranging from 95.03 to 99.98% and atmospheric loadings are about 60 kg/a (Bridle et al. 1984). However, the DE of dibenzofuran was as low as 53.39%. As of September 1986, Burlington's sludge will also be incinerated at the Hamilton incinerator (Yust 1986) which may increase chemical losses.

TABLE 18. Organic chemicals found in wastewater treatment plant effluents from Hamilton and Burlington. There were 208 additional compounds identified in other Ontario effluents that were not observed in this survey (Craig et al. 1984). Concentrations are given in ranges as follows: <1.0 µg/L-A; 1.0-10 µg/L-B; 10-100 µg/L-C; >100; µg/L-D. "-" equals no analysis.

	BURLINGTON	HAMILTON	
Date	Sept. 1979	Sept. 1979	Nov. 1979
VOLATILE COMPOUNDS			
Methylene Chloride	B	B	-
Chloroform	B	B	-
Dichlorobromomethane	A	A	-
Trichloroethylene	A	B	-
Tetrachloroethylene	A	C	-
1,1,1-Trichloroethane	B	C	-
Trichlorofluoromethane	B	-	-
Chlorodibromomethane	B	B	-
Chlorobenzene	-	A	-
1,1-Dichloroethylene	-	D	-
Benzene	A	A	-
Toluene	A	B	-
Ethylbenzene	-	A	-
Hexane	-	A	-
Diethyl ether	B	-	-
Acetone	C	-	-
Carbon disulfide	-	B	-
EXTRACTABLE COMPOUNDS			
Aliphatic hydrocarbons	B	-	-
Decahydro-1,1,7-trimethyl-4-methylene-1H-cycloprop(e)-azulene	A	-	-
Substitute benzenes	-	-	B
Cyclohexyl benzene	A	-	A
1-(t-Butyl)-4-ethenyl benzene	A	-	-
Styrene derivative	-	A	-
Pyrene/Fluranthene	-	-	B
Dichloronitrobenzene	A	-	-
Chloroaniline	A	-	-
Dichloroaniline	-	-	B
Phenol	B	B	A
Bis isopropyl phenol	-	-	A
p-(t-Butyl)phenol	A	-	-
p-Octyl Phenol	B	-	-
p-Nonyl phenol	B	-	-
Trimethyldodecatrienol	-	B	-
Dibenzofuran	-	A	-
tetrahydro-5-methyl-trans-2-furan methanol	B	-	-
1H, 3H-Naphtho(1,8-C,D)pyran-1,3-dione	-	B	A
9H-Fluorenone	-	A	-
7H-Benz (D,E) anthracene-7-one	-	A	-
3-Methyl-2,6-dioxo-4-hexanoic acid	A	-	-
Methyl esters	A	-	B
Misc. Phthalates	A	-	A
Dioctyl phthalate	B	B	C
Misc.-O-containing phthalates	B	A	A
Misc. steroid derivatives	B	-	C
Cholesta-3,5-diene	B	-	-
Cholestan-3-ol	B	-	-
1-(3-Aminophenyl) ethanone	A	-	-
O-Decyl hydroxylamine	-	-	B
Trimethyltridecatriene nitrile	B	-	B
Tetrahydro-naphthonitrile	B	-	-
Methylenepropane dinitrile	-	A	B
1,1'-Biphenyl-2,2'-bicarbonitrile	-	-	B
1-Isocyanatonaphthalene	-	A	-
Amides	B	-	-
N-(p-Methylphenyl)-1-1 aziridine carboxamide	-	A	-
9H-Pyrido (3,4-B) indole	-	B	-
Phenazinol	-	A	-
Imidazole derivative	A	-	-
Methoxyxanthenone	-	A	-
2-Ethyl-4-phenyl-2,1,2,3-oxadiazolin-5-one	A	-	-
N-Butyl-4-methyl benzene sulfonamide	-	-	B
Caffeine	B	B	-

3.3 STORM SEWER AND TRIBUTARY LOADINGS

Storm sewers, while a source of organics (Table 19), are a minor contributor of phenols to Hamilton Harbour. PCBs and pesticides, while released in much smaller quantities, represent a greater proportion of total loading (Table 30). Loading estimates were based on residential test catchments of storm water in Hamilton and Burlington (Marsalek 1978). Results were extended to the whole city of Hamilton and 4741 hectares of Burlington, the area drained by storm sewers discharging to Hamilton Harbour (Dalgarno 1986). The calculated loadings of PCBs from Hamilton storm water account for only 5% of the WTP influent loadings of Shannon et al. (1976). Hence, a source of PCBs in the city, most likely in the industrial area, may contribute the majority to the WTP (Marsalek 1978). Most of the PCB and pesticide loadings are subject to treatment because combined sewage is treated at the Hamilton WTP. However, loadings from the industrial part of Hamilton that periodically overflow directly to the Harbour are not treated. Oil and grease inputs from storm sewers have not been measured.

Table 19. Estimated loadings of organic chemicals from storm sewers (kg/d). (Snodgrass 1981; MOE 1985; Marsalek 1978)

	Hamilton	Burlington
Phenol	1.0	0.1
PCB	0.021	0.002
Pesticides	0.013	0.003

Phenol has been measured in Redhill and Grindstone Creeks but the total loadings were <1.0 kg/d (MOE 1985; Snodgrass 1981; Novak et al. 1981; Holmes 1986), about 2% of the total loadings to the Harbour (Table 32). An OWRC (1967) report cites the Ottawa Street landfill as the source of phenols in Redhill Creek, with an increase in phenol concentrations greater than 10 times the values upstream of the landfill. The Ottawa Street landfill may have received industrial wastes in the past; however, quantities are unknown and likely quite small (Vogt 1986). The sources in Grindstone Creek are unknown but are probably in Waterdown. Oil and grease loadings from tributaries have not been examined; pesticides, PCBs and a few industrial chemicals were below detection limits (MOE 1986c).

3.4 NON-POINT SOURCE LOADINGS

3.4.1 Shipping

Matheson (1958) recommended that discharge of oil and grease in waste waters from ships be prohibited since unmeasured amounts of oil and grease were discharged to Hamilton Harbour in bilge and ballast water. These discharges are now illegal but spills of petroleum products may still occur (Environment Canada 1986). Another unmeasured source of chemicals is the coal washed from the decks of bulk carriers after unloading.

Table 20. Spills to Hamilton Harbour, 1980-1984 (Environment Canada 1986).

Type	Amount (kg)	Site of[1] Spill	% cleaned up on site	Source: Transport (truck/rail/ship)	Source: Industry	Source: Unknown
1980						
solidified wastes	18,100	Red Hill Creek	<30		x	
diesel oil	?	Harbour/discharge	<100	x		
bunker C oil	1,290	Land	100		x	
pine oil	100	Sewer	0		x	
coal tar	700	Harbour	<100	x		
diesel oil	368	Sewer	<30		x	
1981						
hydrochloric acid (65%)	10,900	Harbour	0		x	
diesel oil	184	Storm sewer	0	x		
furnace fuel	368	Land	100		x	
clay slurry	?	Chedoke ck.	0		x	
gasoline	?	Sewer	<100	x		
diesel oil	?	Sewer	<100		x	
diesel oil	?	Harbour	0			x
gasoline	?	Harbour	0			x
ammonium sulfate(4%)	2,300	Harbour	0		x	
1982						
hexane	225	Harbour	<100 (within boom)		x	
soybean oil	900	Harbour	<100 (within boom)		x	
waste oil	?	Harbour	<100			x
bunker C oil	21,500	Harbour	<100 (within boom)		x	
1983						
diesel oil	369	Land/Harbour	<100 (within boom)		x	
varsol	410	Sewer	0		x	
diesel oil	184	Chedoke Ck	<100		x	
plating solution	15,500	Harbour	0		x	
sodium hydroxide(1%)	5,000	Harbour	0		x	
diesel oil	740	Land	0	x		
1984						
tar	4,730,000	Land	100		x	
sulfuric acid(3%)	4,700	Land	0		x	
kerosene	?	Land	0		x	
rolling oil(5%)	4,500	Land	0		x	
sodium hydroxide(2%)	90	Land	0		x	
wash oil	8,200	Land	<100		x	
diesel oil	368	Land and Grindstone Ck	<100	x		

[1] Material spilled on land (or "sewer") would enter storm or sanitary sewers and be treated at the WTP unless heavy rainfall caused combined sewer overflow.

3.4.2. Spills

Spills are a major source of solvents to the Harbour (Environment Canada 1986) and a secondary source of coal tar and oil and grease; inputs of petroleum products ranged from about 1 to 60 kg/d for 1980-84 (Table 20). Of these spills, most are from industry. Although not a continuous loading, spills are high concentration wastes which are often overlooked. Since storm sewer wastes are currently treated, most spills on land will not reach the Harbour unless they occur during heavy rainfall as part of storm sewer overflows.

3.4.3. Atmosphere

Automotive emissions reaching Hamilton Harbour via the atmosphere and road runoff are another source of PAHs. Data on organic chemical emissions and the factors affecting them are abundant (Hampton et al. 1982, 1983); generally, diesel-powered vehicles contribute more PAHs than those powered by gasoline (Handa et al. 1984). Since the Skyway Bridge and QEW are important trucking routes, these inputs could be locally important; to date they have not been measured.

The loadings from rain of PCBs and all pesticides summed together are estimated to be 0.062 and 0.107 kg/a respectively, based on 88 cm of annual rainfall, a total Harbour area of 22 km^2, and rainfall concentrations of PCB and summed pesticides of 32 and 55 ng/L respectively (Strachan and Huneault 1979). These loadings are equivalent to <1.0% of the estimated total (Table 32).

In 1971 a Solid Waste Reduction Unit (SWARU) was built east of Hamilton. Compared to a Toronto incinerator, SWARU emissions of dioxins and dibenzofurans (PCDDs/PCDFs) were 191% higher (Ozvacic et al. 1985). In 3 tests, this incinerator had emissions to the atmosphere of 0.023-0.068 kg/d of dioxin and dibenzofuran (PCDDs/PCDFs), and 0.016-0.078 kg/d of PCBs, chlorophenols (CP) and chlorobenzenes (CB). The proportion of these emissions entering the Harbour is unknown.

3.4.4. Landfill Leachate

Leachate from the Bayview Park landfill in Burlington has been detected up to 3.5 km away from the site; the front and bottom of the plume have not yet been located (Barker et al. 1984). Because the landfill is within 3 km of the Harbour, its leachate may be a source of chemical contamination. Surface drainage of phenols from this site into Indian Creek has been measured at 920 µg/min (≈.001 kg/d) (Benson 1986).

The Burlington landfill is considered a source of leachate to groundwater in the area (Gartner Lee Assoc. Ltd. 1985). Below this landfill, Falcon Creek occasionally exceeds MOE surface water quality objectives for iron and

phenol. Since sample points above the landfill also occasionally exceed the objectives, the contribution by the landfill cannot be estimated. No degradation of Indian Creek water quality by this landfill was observed (Gartner Lee Assoc. Ltd. 1985).

A report on leachate from the Ottawa Street landfill was not available as of September 1986 (Smith 1986).

3.5 LEVELS

3.5.1. Water

3.5.1.1. Phenol

Phenols in Hamilton Harbour water have decreased dramatically from 1958 to 1979 (Table 21). No more recent trends are available since the levels have reached and stayed below 1 µg/L, the detection limit and the current MOE guideline for phenols in water.

Within the harbour, the south shore was clearly the site of highest phenol contamination in the years 1958-1960 7) but after 1972 there were no significant differences among the areas.

3.5.1.2. Oil and Grease

Levels of oil and grease in water have also decreased from 1965 to 1972 (Table 22), apparently by more than 97% in the south shore; no information on levels after 1972 is available. Some of the improvements may be illusory since some oils float while others may be emulsified. The 1965 to 1970 data were based on water samples "near the surface" (HML 1970) while samples in 1972 were taken 1 m below the surface (Nagy 1973). Hence it is likely that both sets of data are biassed by sampling methods.

In 1973, the concentrations of oil and grease in water were nearly uniform at all stations across the Harbour except where Lake-Harbour exchange caused a slight dilution. The overall mean of 0.41 mg/L was representative of water both 1 m from the top and bottom of the Harbour (Nagy 1973).

3.5.1.3. Polynuclear Aromatic Hydrocarbons

No reports of PAH in Harbour water were found in the literature search although MOE (1986e) found high levels of particulate PAH in Lake Ontario near Hamilton (see sections 5.2 and 5.3).

Table 21. Geometric mean concentrations of phenol in water during August of each year (HML 1958; 1959; 1960; MOE 1986b)

Year	Area (see Figure 2)	N	Mean Concentration (µg/L)	95% Confidence Limits
1958	South Shore	12	48	25-90
	East End	4	20	15-27
	North Shore	4	11	5-24
	West End			
	Windermere Basin			
	Central Basin	4	11	5-23
1959	South Shore	3	23	3-177
	East End	1	12	-
	North Shore	1	11	-
	West End	1	5	-
	Windermere Basin			
	Central Basin	1	4	
1960	South Shore	15	37	15-88
	East End	5	3	-
	North Shore	5	4	1-10
	West End	5	5	1-23
	Windermere Basin			
	Central Basin	5	2	-
1972	South Shore	5	2	0.7-3
	East End	2	2	-
	North Shore	2	3	-
	West End	2	1	-
	Central Basin	12	2	0.8-3
1979	South Shore	5	<1	-
	East End	2	<1	-
	North Shore			
	West End	2	<1	-
	Central Basin	10	<1	

Table 22. Geometric mean concentrations of oil and grease in surface water. (HML 1965; 1966; 1970; Nagy 1973)

Date	Area (see Figure 2)	N	Mean Concentration (µg/L)	95% Confidence Limits
Oct. 1965	South Shore	20	14	2-92
	Central Basin	1	0.4	-
Aug. 1966	South Shore	14	3	2-5
Aug. 1970	South Shore	13	4	1-11
Sept. 1970	South Shore	13	5	2-9
June 1972	South Shore	4	0.4	.02-6.7
	Central Basin	6	0.4	.07-2.6
	North Shore	2	0.5	-

3.5.1.4. PCBs and Pesticides

Pesticides and PCBs in water were sampled extensively for the first time in 1982 (Table 23). Gamma-HCH, α-HCH and PCBs were detected 69, 92 and 14% of the time respectively. Gamma-HCH exceeded provincial water quality standards 14% of the time as did PCBs. However, with the detection limit for PCBs at 20 ng/L and the water quality objective at 1 ng/L, it is possible that the PCB objectives were exceeded 100% of the time. However, this was not borne out by levels in sediment and biota (see section 3.5.3).

A more intense sampling of Windermere Basin found PCBs 14% of the time and therefore provincial objectives were exceeded at least 14% of the time (Envirosearch Ltd. 1985). The maximum concentration of PCBs in water was 90 µg/L. There were no spatial or temporal patterns to PCB distribution in Hamilton Harbour, and the high concentration suggests that the probable source was resuspension of contaminated sediments and not WTP effluent.

3.5.1.5. Synthetic Detergents

Large concentrations of the synthetic detergent alkyl benzene sulfonate (ABS) were detected in the Harbour in the 1950's and 60's (HML 1958; 1959; 1960; 1962; 1966; 1968). ABS was thought to reduce iron removal efficiency and interfere with coagulation and sedimentation at the Hamilton WTP. Maximum concentrations of 1.54 mg/L were reported in water samples along the south shore as determined by the methylene blue extraction method. However, the use of ABS in detergents was discontinued in 1968 and levels are no longer measured.

Table 23. PCB's and organochlorine pesticides in 36 samples of surface water, 1982 (MOE 1985)

Parameter[1]	Mean ± SE[2] (ng/L)	Max	Min	Provincial Water Quality Objective (ng/L)	% of samples detected	% exceeding objectives
Total PCB	<20	30	ND[3]	1	14	14
α - HCH	4 ± 0.2	6	ND	-	92	-
β - HCH	< 1	3	ND	-	14	-
γ - HCH	8 ± 2	59	ND	10	69	14
Endosulfan sulphate	< 4	4	ND	-	3	-
Heptachlor epoxide	< 1	1	ND	1	3	0
Oxychlordane	< 2	4	ND	-	6	-
HCB	< 1	4	ND	-	25	-

1 The following were not detected at any time: aldrin, α -and γ -chlordane, dieldrin, methoxychlor, endosulfan I and II, endrin, heptachlor, mirex, DDT and its metabolites.

2 Overall arithmetic mean and standard error (S.E.) of concentration using one-half of detection limit values (prefixed by "<" where necessary).

3 ND = none detected

3.5.2. Sediment

3.5.2.1. Phenols

No information on phenols in sediments was found.

3.5.2.2. Oil and Grease

Oil and grease levels in sediments have decreased from 1972-1978 (Table 24). This change may be even larger, however, since the 1972 figure was based on oven-dried sediment and may have underestimated the quantity of oil and grease due to volatilization. The highest concentrations corresponded to the deepest areas of the Harbour in 1972, suggesting co-precipitation with finer particles. Even though oil and grease concentrations in sediment have decreased by about two-thirds, they still exceed MOE's guideline of 1500 mg/kg for dredge spoil disposal.

Table 24. Geometric mean concentrations of oil and grease in sediments (Nagy 1973; Mudroch and Sandilands 1979)

Date	Area (see Figure 2)	N	Mean Concentration (mg/kg)	95% Confidence Limits
June 1972	South Shore	4	6,800	750-61,000
	Central Basin	6	6,700	2,900-15,600
	North Shore	2	5,000	-
Feb. 1978	East End	7	2,334	1,800-3,014

3.5.2.3. Polynuclear Aromatic Hydrocarbons

PAHs in four sediment samples in 1982 ranged from 1.1 to 43.4 µg/g wet sediment (Table 25). Randle's Reef on the south shore was most contaminated although it improved in a 1985 sample (Zenon 1985). In 1982, the central basin was generally the most contaminated followed by the south shore and Windermere Basin. In a more recent study, Portt et al. (1988) found the highest levels in sediments from the south shore and shipping inlets. The range of concentrations of individual compounds varied over three orders of magnitude across the Harbour. All concentrations in the harbour were greater than in adjacent parts of Lake Ontario by 1 to 2 orders of magnitude (Weiler 1983).

Table 25. Polynuclear aromatic hydrocarbons in sediments (mg/kg dry wt) (Weiler 1983; 1986; Zenon 1985)

MOE Station Number (see Figure 2)	1982				1983
	258(CB)	256(SS)	268(WB)	262(SS)	262(SS)
COMPOUND					
Fluoranthene	12.10	7.30	9.00	43.40	5.06
Perylene	4.30	2.90	2.80	9.70	
Benzo-(k)-fluoranthene	3.20	2.10	2.80	9.00	0.69
Benzo-(a)-pyrene	4.90	2.90	3.10	11.10	4.78
Benzo(g,h,i)perylene	3.60	1.60	2.40	8.60	1.60
Indene(1,2,3-cd)pyrene	3.70	2.20	2.40	9.70	0.39
Naphthalene					2.03
Acenaphthylene					0.33
Acenaphthene					0.40
Fluorene	--- DATA NOT AVAILABLE ---				5.06
Pyrene					4.26
Benzo(b)fluoranthene					4.78
Dibenzo(a,h)anthracene					0.32

3.5.2.4. PCBs and Pesticides

Windermere Basin had the highest PCB concentrations in sediment of the entire Harbour and some samples on the north shore were also highly contaminated. PCB levels in sediment of Hamilton Harbour on a wet weight basis have decreased from 1972 to 1985 in all areas except the east end (Table 26). We do not know if the east end is actually more contaminated now or whether recent samples had a lower percent water relative to other samples. Data on percent water of sediments were not available for all the samples to allow PCB comparisons on a dry-weight basis. Therefore, wet weight data should be interpreted with caution.

Table 26. PCBs in sediment (MOE 1974; 1986b; Envirosearch 1985; Portt et al. 1986)

Year	Area (see figure 2)	N	Concentration (mg/kg wet wt)	Concentration (mg/kg dry wt)
1972	South Shore East End	4	0.54	
	North Shore	1	0.58	
	West End	1	0.80	
	Central Basin	3	0.51	
	Windermere Basin	1	10.10	
1982	South Shore	6	0.312	
	East End	1	0.025	
	North Shore	2	0.912	
	West End	2	0.341	
	Central Basin	7	0.280	
1984	Windermere Basin	15	0.951	
1985	South Shore	7	0.135	0.414
	East End	2	0.105	0.317
	North Shore	2	0.102	0.308
	West End	5	0.075	0.285
	Central Basin	5	0.114	0.401
	Windermere Basin	4	0.278	0.278

A lack of data preclude any trend analyses of organochlorine pesticides in sediment. In 1982, the distribution of pesticides was nearly uniform in the Harbour except for some higher values on the north shore and in Windermere Basin (MOE 1985a). Taking into account the absorption to particulates of pesticides in sediment, one would expect the central basin to be most contaminated. Therefore, there may be sources of pesticides to the north shore, Windermere Basin and the south shore. Storm water runoff is common to all three and household use of pesticides is an input to storm water (Marsalek 1978). The west end of the Harbour is free from any unusual quantity of pesticides in sediments. Compared to PCBs, the concentrations of pesticides are quite low (Table 27).

Table 27. PCBs and organochlorine pesticides in sediments Oct. 1982 (MOE 1985)

Parameter[1]	Mean ± SE[2,3] (mg/kg wet wt)	Range Min.	Range Max.	% of Samples Detected[4]
Total PCB[5]	0.440 ± 0.080	ND[4]	1.270	85
Aldrin	<0.001	ND	0.001	5
α - HCH	0.002 ± 0.0004	ND	0.006	50
β - HCH	0.002 ± 0.0007	ND	0.013	15
α - chlordane	0.005 ± 0.0001	ND	0.018	55
γ - chlordane	0.007 ± 0.0001	ND	0.020	65
oxychlordane	<0.002	ND	0.008	5
op-DDT	<0.005	ND	0.010	15
pp-DDE	<0.001	ND	0.009	25
HCB	<0.001	ND	0.004	25

Note:

1 The following were not detected at any time: γ-HCH, dieldrin, methoxychlor, endosulfan I and II, endrin, heptachlor, mirex, pp-DDD, pp-DDT.

2 Overall arithmetic mean and standard error (S.E.) of concentration using one-half of detection limit values (prefixed by "<" where necessary).

3 Total number of samples = 20

4 ND = none detected

5 The MOE Dredging guideline for PCBs is 0.05 mg/kg. There are no guidelines for the other chemicals.

3.5.3. Biota

There is very little data on organic chemical levels in biota other than fish (Table 28). Chemical levels appear to increase with trophic level, benthic invertebrates having lower levels of PCBs than turtles and birds. The worms also had higher levels of PCBs and other chemicals than associated sediments. However, the sample size was very small and unrepresentative of the entire Harbour.

TABLE 28. Mean concentrations of organic chemicals in biota other than fish (µg/kg)

Chemical	Oligochaetes (dry wt.) (*Tubifex tubifex*) 1985	Associated Sediment (dry wt)	Snapping Turtle Eggs (wet wt) 1984	Tern Eggs 1970	Herring Gull Eggs 1981-82
N	1	1	5	13	10
Dieldrin			60	4,930	221
Endrin					5
Heptachlor epoxide			9.0		85
-HCH					36
-HCH					2.5
Lindane	2.6	0.4			
-chlordane			30		125
Oxychlordane			74		270
-chlordane	13.0	2.3			48
Total DDT	86.8	41.2			7,140
DDE			284	7,230	
Trans nonachlor			20		33
PCB	4,700	1,300	8,590	419,000	49,540
Pentachlorobenzene					18
Total Tetrachlorobenzene					15
HCB	5.8	1.4	22	7,670	
Mirex			84		1,540
Reference	Struger 1986a	Struger 1986a	Struger *et al.* 1986b	Gilbertson and Reynolds 1972	Struger 1986b

Chemical levels in biota should integrate conditions over an area at least as large as their feeding range since both predators and prey can move. Therefore, organochlorine residues observed in a species such as the Herring Gull (*Larus argentatus*) may not be entirely representative of contaminant levels in Hamilton Harbour. Herring Gulls have a feeding range of up to 30 km but feed close (8 km) to the breeding colony during nesting. For colonies in Hamilton Harbour, it is likely that gulls feed in both the Harbour and Lake Ontario. Their prey, smelt and alewife, also move between the Harbour and the

lake at different times of the year (Struger 1986b). Gilbertson (1974) observed that levels of DDE in eggs and breast muscle of common terns nesting in the Harbour increased with season, suggesting that terns accumulated DDE locally. The source of these chemicals would again be both Hamilton Harbour and western Lake Ontario.

Assuming that tern and herring gull eggs are comparable, residues of PCBs and dieldrin have dropped dramatically since 1970 (Table 28). Nevertheless, they remain extremely high.

A wide variety of organochlorine pesticides and PCBs have been detected in the muscle of fish caught in Hamilton Harbour (Table 29); only Aldrin and Heptachlor were not detected. PCB residues declined dramatically, from 2.5 - 11.7 mg/kg in 1976 to 0.02 to 0.49 mg/kg in 1981. Other compounds such as mirex have also declined; most organic chemicals were undetectable or at extremely low levels in 1981. The declines reflect the decreasing use of these chemicals since the early 1970's and declining levels in sediments (Table 26). Up to and including 1979, fish caught in the Harbour exceeded provincial guidelines for safe consumption due to high levels of pesticides (>.3 µg/g) and PCBs (>2 µg/g), but all fish were within guidelines by 1981. The current Guide to Eating Ontario Sportfish is based on 1981 data (MOE 1986f).

PAH compounds have also been detected in edible portions of fish (Table 30) but there are no guidelines regarding consumption of fish containing these chemicals. The levels were much higher relative to the same species sampled in another polluted area, the Detroit River at the confluence of the Rouge River (Hallett et al. 1978).

TABLE 30. Concentrations of polynuclear aromatic hydrocarbons (PAHs) in fillets of fish from Hamilton Harbour and the Detroit River, 1978. (Hallett et al. 1978)

Location	Species	N	Mean PAH Concentration (ng/kg)			
			Perylene	Benzo (k) Fluoranthene	Benzo (a) Pyrene	Coronene
Hamilton Harbour	Carp	9	25.47	8.16	50.7	182.98
	Pike	10	18.48	7.43	28.77	65.83
Detroit River	Carp	10	0.11	0.08	0.12	0.84
	Pike	10	13.05	1.57	17.34	24.26

Table 29. Organic chemicals in fish muscle (fillets mg/kg wet weight) (MOE 1974; 1986d; Cairns 1986)

YEAR	SPECIES	N	LENGTH (cm)	WEIGHT (gm)	PCB	HCB	α-BHC	LINDANE	β-BHC	HEPTACHLOR	MIREX	DIELDRIN	ALDRIN	pp-DDE	pp-DDT	pp-DDD	pp-DDT	TOTAL DDT	α-CHLORDANE	γ-CHLORDANE
1972	Brown Bullheads	5			3.960	0.028						0.008		0.400	0.006	0.150		0.556	0.184	0.046
	Alewife	1			3.500	0.060						0.020		0.470	0.070	0.140		0.680	0.040	0.030
	White Perch	11			5.773	0.096						0.026		0.662	0.022	0.346		1.030	0.237	0.043
	Gizzard shad	24			3.925	0.052						0.021		0.472	0.006	0.396		0.874	0.146	0.046
	Goldfish	1			11.700	0.070						0.090		0.126	0.040	0.102		0.232	0.610	0.470
	Sunfish	1			2.500	0.010						Tr		0.130	0.010	0.090		0.230	0.090	0.020
1976	Smelt	39	16.9	32	2.055						0.152									
	Chinook	4	51.5		2.263						0.159									
	Alewife	2	15.9		3.550						0.185									
	Yellow Perch	2	22.9	71	0.520						ND									
	White Perch	2	16.5	43	2.100						ND									
	Carp	2	56.5	2519	8.850						ND									
	Red Horse Sucker	5	36.3	607	1.750						0.001									
1978	Carp	6	57.7	3875	1.673	0.006	0.003	0.003	0.0005	ND[2]	0.051		ND	0.099	0.044	0.237	0.026	0.408	0.083	0.076
	White Perch	20	23.0	294	1.134	0.002	0.0038	0.0027		ND	0.036		ND	0.093	0.044	0.217	0.054	0.409	0.069	0.062
	Brown Bullheads	18	27.5	277	1.132	0.002	0.0044	0.0008	0.0005	ND	0.044		ND	0.094	0.017	0.119	0.018	0.250	0.026	0.039
	Coho Salmon	4	53.4	1375	0.875	0.008	0.002	0.0033	ND	ND	0.129		ND	0.089	0.048	0.107	0.069	0.314	0.028	0.034
	Chinook Salmon	2	75.0	4350	1.330	0.014	0.012	0.009	0.008	ND	0.200		ND	0.075	0.119	0.260	0.177	0.631	0.088	0.109
	Smelt	20	16.6	28	0.989	0.008	0.006	0.0052	0.0073	ND	0.163		ND	0.106	0.058	0.114	0.083	0.362	0.020	0.030
	Lake Trout	2	51.5	1000	2.195						0.290									
1979	Lake Trout	1	51.0	1500	7.736	ND[2]		0.041	0.006	0.009	ND	0.091	ND	0.678	0.168	0.161	0.346	1.353	0.204	0.224
	Coho Salmon	5	54.0	1650	1.517	ND	0.014	0.0026	0.003	ND	0.037		ND	0.134	0.032	0.037	0.047	0.251	0.045	0.033
	Smelt	10	15.5	22	1.240	0.042	0.0095	0.0017	0.0023	ND	0.066		ND	0.250	0.031	0.035	0.044	0.361	0.046	0.021
1980	Spottail shiner	7	4.7		0.229	0.0004	0.0027	ND	ND	ND	0.001		ND	0.037	ND	0.002	ND	0.039	0.006	0.007
1981	Pike	9	65.2	1433	0.489	0.0004	0.0001	ND	ND	ND	0.012		ND	0.054	0.006	0.014	0.004	0.079	0.004	0.008
	Carp	6	53.0	1992	0.022	ND	ND	ND	ND	ND	ND		ND	0.001	ND	ND	ND	0.001	ND	ND
	Brown Bullheads	2	28.0	290	0.041	ND	ND	ND	ND	ND	ND		ND	0.0005	ND	ND	ND	0.0005	ND	ND
	Yellow Perch	2	12.0	20	0.106						0.004									0.004
	White Perch	8	17.3	66	0.421	0.0011	0.0011	0.0022	0.0016	ND	0.002		ND	0.032	0.005	0.024	0.002		0.009	0.005
	Pumpkinseed	1	13.0	50	0.022															
1984	White Suckers [1]	18	42.2	885	1.520	0.014				.0065	.062	0.017						0.335	0.0040	

[1] Whole fish

[2] ND = Not detected

4.0 THE POTENTIAL EFFECTS ON AQUATIC BIOTA OF CHEMICALS IN HAMILTON HARBOUR

4.1 Factors Affecting Chemical Toxicity

The preceding review has demonstrated the presence of metals and organic chemicals in effluents, water, sediments and biota of Hamilton Harbour. However, the mere presence of these materials in an aquatic environment does not mean that there are adverse effects on aquatic biota. For adverse effects, there must be accumulation of chemicals by biota plus toxicity (an adverse reaction between a chemical and a biological tissue). Many chemicals may be present but not taken up, i.e. they are not 'biologically available'. Similarly, a given level of chemical in biota may not always have the same effect. The following is a review of factors affecting the biological availability and toxicity of chemicals.

Most data reporting the accumulation or toxicity of chemicals to biota are based on controlled laboratory tests in filtered water of constant composition, under conditions of constant temperature, photoperiod, and feeding regimes. Test organisms are chosen for their uniformity, availability from commercial suppliers, and their good health. Toxicity tests do not include competition or predation from other organisms, realistic fluctuating exposure regimes, simultaneous exposure to disease or other chemicals, or stresses due to natural variations in environmental conditions (e.g. low dissolved oxygen levels). Therefore, toxicity test data are only bench-marks against which to compare conditions; the probability that toxicity will occur under any given condition in the harbour can only be estimated.

Conditions in the Harbour which reduce the effects of chemicals are mostly related to exposure. These include:

- dilution: A chemical exposure sufficient to cause accumulation and toxicity may be prevented by rapid circulation and mixing within the Harbour. Given the rapid turnover in the Harbour due to intrusion by lake water, it is likely that most wastes are rapidly diluted below acutely toxic concentrations;

- complexation and precipitation of chemicals to sediments: Organic particulates, both biotic (bacteria and algae) and abiotic (waste discharges), will bind waterborne chemicals and reduce their uptake by aquatic biota. Starodub et al. (1987) have demonstrated that organic complexing agents extracted from Hamilton Harbour sediment can significantly reduce metal toxicity to algae. The precipitation of chemicals to sediments may, however, affect benthic organisms (see below);

- low dissolved oxygen concentrations in hypolimnetic waters: Fish avoid deeper parts of the Harbour during summer months since oxygen levels can decrease to below 1.0 mg/L (Portt et al. 1988). Since chemicals bound to particulates accumulate in deeper areas, chemical exposure of fish is prevented.

There are also conditions that will enhance exposure and toxicity. These include:

- precipitation to the sediments: The complexation and precipitation of chemicals by particulates causes sediment enrichment. This is also the case for lipid-soluble organic chemicals which can partition into oil and grease. The results are high levels of chemicals in sediments and unavoidable exposure of benthic organisms. Invertebrate populations are severely affected in deeper parts of the Harbour due either to high levels of chemicals or to low dissolved oxygen (Portt et al. 1988). The consumption of benthos by benthic-feeding fish can transfer chemicals directly to fish; ingestion of sediments or disturbance of pore water enriched with chemicals will also expose these fish to chemicals;

- life stage of the organism: Migrating adults and larval organisms that drift with currents may be exposed to higher levels of chemicals than those that seek littoral habitat in parts of the harbour distant from industry. A good example is the attraction of large numbers of adult fish to heated effluents. Large schools have been observed feeding in winter near heated effluents on the south shore of the Harbour (Cairns 1986). While these effluents may be primarily cooling water, the fish are spending considerable time in areas contaminated with other effluents;

- biomagnification: The data on chemicals in biota illustrate that persistent chlorinated chemicals increase in concentration with position in the food chain. Those at the top (birds) are very contaminated, even when levels in the water appear relatively low. Since persistent organic chemicals are poorly excreted, the birds contain almost all of the chemicals accumulated by their prey. The opposite process, biominification, occurs with metals, i.e. concentrations decrease up the food chain (Luoma 1986). Exceptions to this pattern are the organomercurial compounds that behave like chlorinated organics.

- other stresses: Natural diseases, competition, predation, reproduction, migration and environmental variation all may stress the biota of Hamilton Harbour and enhance their response to chemicals. Important stressors in the Harbour include low dissolved oxygen levels during much of the summer, exotic species, and destruction of habitat (Holmes 1986);

- mixtures: Chemicals do not occur singly; mixed effluents may contain hundreds of separate chemicals. The potential for mixture interaction is reviewed below.

4.2 The Effects of Specific Chemicals

The following are brief resumes of chemical effects on organisms. They are derived primarily from literature reviews in support of water quality criteria or objectives. They provide a bench-mark for judging the levels of chemicals in water that are toxic to various species of aquatic biota and the degree to which chemicals bioaccumulate. Based upon the above discussion,

they should not be regarded as the definitive description of chemical effects in Hamilton Harbour. The implications of chemical exposure can only be truly assessed by direct measurement of chemical effects *in situ*.

4.2.1. Arsenic

Arsenic (As) in fresh water exists predominantly as arsenite (As (III), 40%) and arsenate (As (V), 60%), the As (III) form being the more toxic to aquatic biota (Doyle *et al*. 1978). A pH above 7.0 and high dissolved oxygen levels will increase the proportion of As (V) compounds; As (III) compounds should predominate in the anoxic hypolimnetic water and sediments of Hamilton Harbour during the summer. Roughly half the arsenic entering a waterbody remains in solution while the remainder accumulates in sediments. Since iron oxides can enhance As precipitation (Canviro 1986), a greater proportion may be in Hamilton Harbour sediments. However, the shifts in redox potentials associated with anoxic conditions during the summer may cause a release of arsenic back into the water column (Canviro 1986).

Arsenic is readily taken up by biota and can be excreted. Transformations can also occur, with methylation by bacteria and algae very common (Wong *et al*. 1977; Baker *et al*. 1983). The result will be a loss of arsenic from the system through volatilization. Another consequence is that the majority of arsenic found in biota is in an organic form, often stored in lipid.

The IJC Water Quality Objective for total arsenic is 50 µg/L to protect raw water for public water supplies (IJC 1977); the measured toxicity of all forms of arsenic to aquatic biota suggests that this objective should afford a wide safety margin (IJC 1977; Canviro 1986). The acute toxicity of arsenic to algae is between 2000 and 10 000 µg/L, a range encompassing lethal levels for invertebrates and fish and detrimental effects on benthic invertebrate and bluegill sunfish populations in treated outdoor ponds. Chronic toxicity to invertebrates occurred at about 520 µg/L, growth of fish was reduced at 6000 g/L and learning behavior of fish was affected at about 100 µg/L. This was the lowest effect level tested, and it was twice the IJC objective. Since arsenic levels in water average 1 µg/L in Hamilton Harbour, it appears that toxicity is unlikely.

The significance of arsenic residues in sediments (5–25 mg/kg dry wt, Table 12) is unknown since we found no research specifically on sediments. However, one study reviewed by IJC (1977) reported arsenic residues in biota of a pond treated with 4000 µg/L. Most of the arsenic was deposited in sediments, and biota accumulated very high concentrations (e.g. 1.3 µg/g in muscle of fish). It is possible that the arsenic in fish was taken up from sediments rather than from the water. This is the case with selenium (Hodson *et al*. 1984), an element whose chemistry is closely related to arsenic.

The accumulation of arsenic by freshwater organisms shows a negative food chain accumulation, i.e., there is biominification. The BCF for fish ranges from <1 and 30, but there are few good measurements (IJC 1977, Canviro, 1986).

4.2.2. Cadmium

Cadmium is not a nutrient, unlike copper or zinc. According to a review by Eisler (1985), it is readily accumulated by aquatic organisms, with levels increasing in proximity to sources such as urban or industrial development. Cadmium is concentrated in the viscera of fish, particularly liver and kidneys, and levels increase with age. Levels in muscle (edible portions) are generally 2 to 10 times less than in liver.

The significance of cadmium levels in Hamilton Harbour is almost impossible to assess. Levels of cadmium that are acutely lethal to most aquatic biota are as low as 0.8 to 10 µg/L while levels of 0.2 to 10 µg/L may impair growth, development and reproduction of invertebrates and fish during chronic exposures (Eisler 1985). Since the average level of waterborne cadmium in Hamilton Harbour is 0.3 µg/L, toxicity may be occurring, although the net balance between factors enhancing or mitigating metal effects are unknown. If there is an effect of cadmium, it is likely to be small and difficult to detect since levels are so close to threshold values for sublethal toxicity and since so many other factors affect biota. It is clear, however, that levels of cadmium in the Harbour need to be measured with lower detection limits and a high degree of accuracy. The most sensitive indicator of effects may be the degree of bioaccumulation in biota, particularly in tissues such as liver and kidney.

The BCF of cadmium is relatively high (4900) for tissues such as liver of rainbow trout exposed chronically. The BCF for muscle is not well-defined but whole body residues associated with acute mortality in fish are about 5.0 mg/kg wet weight, a concentration well below the lethal level for avian or mammalian predators (Eisler 1985). It is likely that fish would die before accumulating a dose lethal to wildlife. The significance of sediment cadmium concentrations is unknown.

4.2.3. Chromium

Chromium (Cr) in water exists either as Cr (VI) or, more commonly as Cr (III). Under conditions of high organic carbon and low dissolved oxygen, Cr (VI) is converted to Cr (III) which, in turn, is hydrolyzed and is present as a particulate or colloid (Holdway 1987). While the toxicity of chromium varies with valence state (Cr (VI) is more readily taken up but less toxic than Cr (III)), only total chromium is usually measured in surveys. Nevertheless, even if all chromium in Hamilton Harbour was in the most toxic form, the levels would still be considered "safe".

The current IJC Water Quality Objective is 50 µg/L of total chromium to protect raw water for public water supplies (IJC 1977). Effects on most aquatic biota do not become evident until levels exceed 100 - 150 µg/L, well above the average of 6 µg/L observed in the Harbour. Levels that are acutely lethal generally exceed 5000-10 000 µg/L (Holdway 1987). However, prolonged exposure of duckweed (Lemna minor) and Daphnia magna to as little as 10 µg/L of Cr^{6+} inhibited growth (Eisler 1986a). Eisler's (1986a) review also reported similar effects on rainbow trout (Salmo gairdneri) and chinook salmon (Oncorhynchus kisutch) at 16 - 21 µg/L after 14 to 16 weeks of exposure. The toxic effects of chromium may be due either to effects on gills, respiration and osmoregulation, or on glucose metabolism (Holdway 1987). Chromium is an essential nutrient for most animals and is a co-factor of insulin.

Chromium does not bioaccumulate from water to any extent in fish muscle (BCF<3; Holdway 1987) and mammalian tolerance for orally ingested chromium is quite high (IJC 1977). Chromium accumulation from sediments (via food) by benthic feeding fish is greater than accumulation from water. However, it is unlikely that chromium will cause food chain effects through biomagnification since surveys have demonstrated biominification (Holdway 1987).

No information was found to interpret the significance of the levels of chromium in sediments, although uptake by fish occurs. Since chromium may induce tumors in mammals, Holdway (1987) speculated that it may be involved in tumor induction in Hamilton Harbour fish.

4.2.4. Copper

Copper is a micronutrient for most organisms, e.g. as an essential component in some metalloenzymes and in respiratory pigments of invertebrates. Hence, it is readily taken up from water, retained when supplies are limited, and actively stored or excreted when intake rates approach toxic levels.

Levels of copper in water that are lethal to aquatic biota range from 5 - 65,000 µg/L (invertebrates) and 20 - 10,000 µg/L (fish) (Hodson et al. 1979) due to wide ranges in the sensitivity of the species tested and in the chemical characteristics of the test solutions. High organic and inorganic complexing capacity of the test water can reduce the availability and toxicity of copper to very low levels.

Copper is used as an algicide, and toxicity to algae also varies widely due to water quality. Photosynthesis of algae can be inhibited by as little as 5 µg/L, but generally only in very dilute systems with little complexing capacity. Oxygen evolution, respiration, cell morphology, reproduction and growth rates are affected at copper levels between 5 and 300 µg/L, as is nitrogen fixation by blue-green algae.

Chronic effects of copper on invertebrates are evident at concentrations greater than 5 - 10 µg/L and include adverse effects on rates of mortality, growth and reproduction. Newly hatched organisms are generally more sensitive than eggs or adults, and resistance increases with body covering (e.g. impermeable exoskeletons) or use of an operculum, as in the case of some snails. This is one of many behavioral responses to copper which may also include reduced pumping and feeding rates by bivalves and distress wriggling, impaired reaction to food and changes in diurnal vertical migrations of other invertebrates.

Copper toxicity to fish during chronic exposures affects rates of reproduction, growth and mortality. These effects occur between 5 and 40 µg/L in water low in organic materials and between 66 and 120 µg/L in organically enriched waters. Aspects of reproduction affected include egg production, spawning frequency, egg mortality and survival of larvae. The extent of effect is again a function of the species and life stage tested and of the water quality. Surprisingly, the length of exposure may not be important since reproductive effects in fathead minnows occurred even after short-term exposure of maturing females. The incidence of disease in fish is also affected by as little as 30 µg/L copper, either by increasing the virulence of pathogens or by decreasing host resistance of fish. Fish can avoid copper, detecting levels as low as 4 µg/L. They may also become hyperactive, cough more frequently (an action to clear the gills of irritants) and show a classical stress response when first exposed. The toxic action of acute copper poisoning includes major disturbances in ionoregulation, primarily by gills, but kidney lesions have also been observed.

Acclimation to copper by fish is also possible and related to synthesis of metallothionein, a metal-binding protein.

Applying these data to Hamilton Harbour, it is obvious that the high frequency of waterborne copper levels in excess of the IJC Water Quality Objective (5 µg/L; IJC 1978) may pose a danger to aquatic biota. The levels are within the range causing chronic or sublethal effects on aquatic biota. The lack of exposure-time dependency of copper effects on reproduction also means that even brief elevations in copper may be significant. Hence, if copper is available to biota, there should be reductions in primary productivity, changes in population structure of invertebrate communities, reduced reproduction in fish and enhanced rates of disease. Research is needed to demonstrate whether copper is, indeed, available, since there appear to be abundant organic particulates for copper complexation (Threader et al. 1988).

The levels of sediment copper are generally below those associated with reduced populations of benthic invertebrates. Kraft and Sypniewski (1981) found a correlation between the copper content of sediments in the Keewanaw Waterway and the numbers of invertebrate species and total organisms per square metre. Invertebrates were less common when sediment copper exceeded 300 µg/g. In Hamilton Harbour the central basin exceeded this value once (1980, Table 12), but all other measurements were much lower.

4.2.5. Iron

Iron is discharged to the Harbour in amounts that far exceed those of other chemicals, and average waterborne concentrations in the Harbour are 220 µg/L. Therefore, a significant proportion of measured values will exceed the Great Lakes Water Quality Objective for iron of 300 µg/L (IJC 1978). The objective was set to protect aquatic biota, but this is based not on a chemical toxicity, but rather on the physical effects of very specific sizes of iron flocs. Iron effects on aquatic ecosystems are most often associated with acid mine drainage. Iron in acidic solutions becomes a hydroxide floc as acidity is neutralized in receiving waters. At high concentrations of iron, this floc is large and non-toxic, but at concentrations of about 1500 µg/L, the floc is very fine and can kill fish and fish eggs by smothering respiratory surfaces. The IJC objective is intended to limit floc formation under these conditions. Since the majority of iron currently entering the Harbour is in neutral effluents, it is unlikely that these conditions will occur.

This conclusion is supported by Loeffelman et al. (1985). They compared iron concentrations in water to effects on aquatic biota in a variety of field and laboratory studies. Acute and chronic toxicity could only be observed at total iron levels greater than 1000 µg/L. The toxicity was most closely related to concentrations of ionic Ferrous (II) iron; other species were most often complexed or present as colloids. Healthy aquatic communities were often observed at total iron levels in excess of 10,000 µg/L.

Iron in water will likely co-precipitate to sediments with anions such as phosphate and with organic detritus. Based on the high concentrations in sediment of both Hamilton Harbour and the western end of Lake Ontario (see Tabel 35, section 5.1), it is obvious that this process is going on. There are potential benefits and problems associated with high sediment iron levels. Lum and Gammon (1985) reported a strong positive correlation of metal levels in sediments with levels of iron oxides, which supported the idea that the release of metals from sediments was controlled by a strong sorption capacity of hydrous iron oxides. Therefore, it is likely that iron-rich aerobic sediments in Hamilton Harbour will protect aquatic biota from exposure to other toxic metals. This may, in fact, explain why fish from Hamilton Harbour have relatively low blood lead concentrations (Section 2.5.3), even though the sediments are quite contaminated relative to other Harbours (Table 34).

The negative aspect of high sediment iron levels is the smothering action by high rates of precipitation (Loeffelman et al. 1985). This has been observed in streams but may not apply in lentic environments where benthos are adapted to living in soft sediments formed by continual precipitation of material from the water column. The net effect of iron on sediments is therefore likely to be beneficial.

4.2.6. Lead

Lead is discharged to the aquatic environment in two main forms: inorganic lead (as lead salts) and, very rarely, as organolead compounds, usually from the manufacture or use of alkyllead compounds as gasoline additives.

Inorganic lead is rapidly precipitated to sediments by organic and inorganic complexing agents. Algae, for example, have extremely high bioconcentration factors for lead, up to 20,000 (Hodson 1986). The result is a continual enrichment of sediment lead, as shown by core profiles. Bioconcentration factors of inorganic lead decrease with increasing trophic levels, demonstrating biominification (Luoma 1986).

Both waterborne and sediment lead are biologically available; in laboratory exposures, accumulation in biota is a direct function of exposure level. However, the processes that cause lead precipitation and enrichment in sediments also reduce uptake from water by biota, so that high organic and inorganic complexing capacity will reduce both lead uptake and toxicity. Uptake of sediment lead is also affected by various processes that are only poorly understood. The accumulation of lead by benthic invertebrates is inversely correlated to the levels of sediment iron (Luoma 1986), but prediction of lead accumulation by biota is difficult. Campbell and Tessier (1986) reviewed various extraction techniques that estimated levels of lead dissolved in interstitial water and lead bound to particulates in sediments. In some cases, estimates of dissolved lead were strongly correlated with lead levels in biota, and in others only total sediment lead levels were well correlated. It appears that the best measure of biologically available lead will be direct measures of lead in the biota (Luoma 1986); blood lead levels of benthic fish sampled from Hamilton Harbour were generally less than in other harbours around Lake Ontario (Section 2.5.3).

Lead toxicity to biota varies with exposure, i.e. with the amount of uncomplexed lead in water or sediment. Hence, reported values for acute toxicity vary widely. The ranges for algae are 10 - >100,000 µg/L, but include both lethal and sublethal effects, since most algal assays measure responses such as reduced productivity. The most sensitive response at 10 µg/L was reduced productivity of phytoplankton in Lake Ontario water; this test was quite realistic since natural levels of complexing agents were present.

Zooplankton are killed by lead levels ranging from 280 to 71,000 µg/L, but chronic toxicity occurs at levels as low as 30 µg/L. Integrating the effects of lead on long-term rates of growth, reproduction and mortality, Borgmann et al. (1978) showed that 48 µg/L of lead could significantly reduce biomass production rates of snails. Behaviour may also be impaired; zooplankton changed their response to light at lead levels as low as 1.3 µg/L, and this may cause altered energy transfer within food webs (Wilson and Roff 1981).

The acutely lethal concentration of lead for fish varies from 200 to 542,000 µg/L, with water quality (complexing capacity) and species being the dominant factors affecting responses. Chronic lead toxicity resembles that in humans, involving both hematological and neurological damage, and it can be related to levels of lead in both water and tissues. The threshold exposure concentration causing these effects is as low as 5 µg/L, while the threshold level of blood lead is about 300 µg/L.

The effect of lead on fish and aquatic biota, after adjustment for the mitigating effects of hardness (inorganic complexing capacity), formed the basis for the IJC Water Quality Objective for lead in Lake Ontario of 5 µg/L (IJC 1980). The average level of waterborne lead in the Harbour was also 5 µg/L (Table 11), indicating that a large fraction of lead measurements exceeded the objective. However, due to complexation, lead is unlikely to be a problem. None of the fish sampled in Hamilton Harbour by Hodson et al. (1983) had blood lead levels exceeding 300 µg/L but the levels were slightly elevated above those of lake trout from the open waters of Lake Ontario, indicating low levels of contamination. Since benthic-feeding fish species were more contaminated than those feeding in the water column (e.g. white perch, Table 13), the likely source was the sediments which appear highly contaminated. Studies of other ecosystems contaminated with lead demonstrate that high levels of sediment or waterborne lead can contaminate fish, often to levels exceeding both the threshold for toxicity to fish and the WHO recommended limit for lead in fish for human consumption (Hodson 1986).

Organic lead compounds may be formed naturally, through biological or chemical processes of methylation in sediments (Chau and Wong 1978), or they may be discharged during manufacture or use (Chau 1986). Methylation processes, while they appear to occur, do so at very low rates and are probably an insignificant contributor to lead cycling. Industrial production of alkyllead compounds does not occur in Hamilton, but there is sufficient use that spillage and evaporation of gasoline may lead to some contamination. No analyses for these compounds have been made in Hamilton Harbour.

Sediment contamination (Table 12) exceeds the level considered harmful for marine organisms. Chapman (1986) created a marine sediment assessment scheme that measured levels of sediment chemicals, sediment toxicity in lab tests and health and population status of benthic organisms in contaminated sediments of Puget Sound (see also discussion of PAH's). The three types of data were combined in an index that suggested adverse effects on biota at sediment lead levels greater than 50 µg/g (dry wt). The same index predicted that sediment levels of PAH and PCB in excess of 3.8 and 0.1 µg/g (dry wt), respectively, should adversely affect marine benthic organisms.

Assuming Chapman's (1986) conclusions could be applied to Hamilton Harbour, one cause of the low diversity of benthos in the Harbour (Portt et al. 1988) may be these three chemicals.

4.2.7. MERCURY

The levels of mercury in Hamilton Harbour water are well below the Great Lakes Water Quality Objective of 0.2 µg/L (IJC 1977). The levels in fish fillets are also below the guidelines for consumption of 0.5 µg/g wet weight. The intent of the objective, which is to limit the contamination of fish, has therefore been met in the Harbour. Since contamination of fish occurs at waterborne mercury levels below those causing toxicity (generally greater than 1 µg/L), aquatic biota should be protected from toxicity.

The toxicity of dietary mercury to wildlife also would occur at levels far exceeding those found in the flesh of Hamilton Harbour fish. Since high levels of mercury are found in fish-eating birds nesting on Hamilton Harbour, it is likely that the source is from food consumed outside the Harbour.

4.2.8. NICKEL

The average levels of nickel in Hamilton Harbour water are 10 µg/L, above those of Lake Ontario (Table 33) but well below the Great Lakes Water Quality Objective of 25 µg/L. This objective is based on the projected chronic toxicity of nickel to Daphnia magna reproduction; the threshold is about 25 µg/L (IJC 1978). This is by far the most sensitive response since concentrations causing acute lethality for most aquatic organisms exceed 1,000 µg/L. The chronic toxicity of nickel to fish occurs at about 700 µg/L of nickel. No data were found to judge the significance of sediment nickel concentrations.

4.2.9. ZINC

Zinc is a micronutrient for most organisms. As Spear (1981) has shown in a thorough review, zinc may be accumulated readily by aquatic biota, but mechanisms are present for its rapid elimination. As with other metals, zinc concentrations are highest in the lowest trophic levels, i.e. aquatic bacteria and plants. Algae, periphyton and rooted aquatic plants contain about 20 to 150 µg/g (dry wt) in normal circumstances, and up to 100 times more in zinc-contaminated areas. Invertebrates may contain 50 - 300 µg/g (dry wt) and fish 20 - 100 µg/g. In polluted areas, levels of zinc are elevated in livers of fish, but levels in muscle are only slightly elevated. Since fish are predominantly composed of muscle, whole body residues do not reflect zinc contamination very well.

Aquatic plants will respond to as little as 15 µg/L of zinc, but most are affected only above 100 µg/L and some can tolerate up to 10,000 µg/L. Tests by Dr. Paul Wong, Great Lakes Laboratory for Fisheries and Aquatic Sciences, have shown that the IJC Water Quality Objective of 30 µg/L may not protect phytoplankton of the Great Lakes from toxicity. His bioassays were conducted with natural populations incubated in lake water, thereby representing realistic levels of metal complexation and toxicity (Wong, personal communication). Aquatic bacteria are relatively more resistant than algae, although the number of tests reported are fairly small (Spear 1981).

The median lethal concentrations of zinc for aquatic invertebrates vary from 72 to 60,000 µg/L, depending upon water quality and the species tested. Highly resistant species are often those with a hard exoskeleton or, in the case of some snails, an operculum that can be closed when conditions are unfavorable. Studies of reproduction in Daphnia magna have estimated that reproduction would drop to 16% of controls in the presence of 70 µg/L of zinc. Metallic zinc ingested by snails was also observed to inhibit their reproduction in aquaria studies. Behavior is very sensitive to zinc, snails showing evidence of 'distress' at concentrations of 50 to 100 µg/L. Some limited experiments have also shown that avoidance is possible.

Zinc lethality to fish varies considerably, from about 70 to 40 000 µg/L due to water quality (organic and inorganic complexation), species tested, and life stage tested. The most sensitive species are the salmonids, the most resistant the percids, and cyprinids are in between. Spear (1981) provides figures and equations developed from an extensive compilation of published data that allow the prediction of toxicity for fish from these three orders of fish at any hardness (= inorganic complexing capacity). The most sensitive life stage appears to be immediately post-hatch (alevin or larval stage) when the fish have high metabolic rates per unit of body mass, large developmental changes are occurring, and there is rapid uptake of waterborne ions.

Sublethal toxicity of zinc to fish includes impaired spawning, decreased egg production, and reduced hatchability, effects occurring at levels as low as 20 µg/L. This high sensitivity was typical of salmonid eggs. Other species were more resistant with thresholds of toxicity usually above 50 µg/L. Field studies indicate that reproduction of fish near Flin Flon, Manitoba was unaffected by up to 90 µg/L of zinc, but 300 µg/L may have caused recruitment failure. Growth is also affected and there are a variety of physiological responses to zinc exposures, but they are usually induced by much higher levels than affect reproduction.

Relative to zinc levels in Hamilton Harbour (average of 30 µg/L, Table 33), the concentrations harming most aquatic biota are quite high. Only rarely would waterborne zinc reach levels that cause chronic toxicity, and it is very unlikely that lethality would be observed, except in the case of a spill. A possible exception would be the inhibition of algal growth rates during periods of high zinc concentration. The significance of the lost productivity would depend on the duration and extent of contamination.

The significance of sediment zinc levels is unknown, but concentrations are much higher than in any other part of Lake Ontario (Table 34). Studies are needed to determine whether benthos would be affected under conditions similar to those in the Harbour.

4.2.10 AMMONIA

Ammonia data were not included in this review because loading and distribution within the Harbour have been reviewed by Threader et al. (1987); they did not, however, review toxicity in water, ammonia dissociates to form NH_4^+, an ion that is considered relatively non-toxic; undissociated (unionized) ammonia is the toxic form. Dissociation, however, is not complete, but increases with pH and temperature. Hence, at any given pH or temperature, the percent unionized ammonia can be calculated from the dissociation constant. The rationale for the Great Lakes Water Quality Objective of 20 µg/L unionized ammonia (IJC 1978) provides convenient tables for estimating the percent undissociated. At a Harbour pH of 7.5 - 8.0, the maximum amount of unionized ammonia is 5%, assuming a temperature of 20-25° C. These conditions prevail in August when total ammonia averages 150 µg/L (Threader et al. 1987); the estimated level of undissociated ammonia is therefore 8 µg/L. Since this is an average figure, levels may periodically exceed the objective. Ammonia levels are highest in the late Spring (Threader et al. 1987) when temperatures are about 3-5° C. At a total ammonia level of 2500 µg/L, the concentration of unionized ammonia should be about 10 - 30 µg/L. Levels at other times of the year are similar.

The acute toxicity of ammonia occurs at concentrations of unionized ammonia of 200 µg/L or greater. Sublethal pathology and effects on growth of fish have been observed at levels as low as 20 µg/L after prolonged exposure. Therefore, the ranges of concentrations in Hamilton overlap the levels that are chronically toxic to aquatic biota.

4.2.11. CYANIDE

Free cyanide in water is readily taken up by fish and is highly toxic. Lethal thresholds are 50 µg/L or higher, while sublethal and chronic toxicity affecting growth, reproduction and performance was measured at waterborne levels as low as 18 µg/L. These data support a Great Lakes water quality objective of 5 µg/L. Cyanide levels in Hamilton Harbour water are uniformly less than 1 µg/L so that effects on fish are unlikely. The sensitivity of other biota is unknown.

4.2.12. POLYNUCLEAR AROMATIC HYDROCARBONS

PAHs are fused, multi-ringed compounds consisting primarily of carbon and hydrogen (Eadie 1984; Hallett and Brecher 1984). While generally of very low water solubility, they are readily taken up by aquatic biota due to high lipid solubility. However, they do not accumulate to high levels in most vertebrates due to the presence of metabolizing enzymes, collectively known as the mixed function oxidase (MFO) system. Some invertebrates have this enzyme system while others do not; the latter species may accumulate PAH to very high levels (Roubal et al. 1987). Hence, the observation that fish from Hamilton Harbour had measureable levels of PAH in muscle tissue indicates a high degree of environmental contamination; the fish reflect the high loading rates and high degree of sediment contamination by PAH (Tables 33 and 35).

There is little acute lethality associated with exposure to PAH compounds. Because solubility limits rates of uptake and metabolism limits accumulation, few reach levels in tissue high enough to kill fish quickly. There is one important exception however: fish that have taken up a non-lethal dose of anthracene may be killed by a subsequent exposure to sunlight; phototransformation of anthracene in the skin and muscle creates a highly toxic derivative (Leversee et al. 1983; Oris and Geisy 1986). This phenomenon may also occur with other PAH, but has not been well studied in aquatic organisms.

The most important effects of PAH are carcinogenesis. This process is initiated by the MFO system, the same group of enzymes that facilitates PAH excretion through addition of oxygen or hydroxyl groups to the ring structures. The new compounds include epoxides and dihydrodiols which are highly carcinogenic to mammals. The carcinogenicity of some PAH, in particular benzo(a)pyrene, has been demonstrated in fish.

While the loading of PAHs to Hamilton Harbour and their presence in sediments and fish have not been proved to cause cancer in fish, there is strong circumstantial evidence that this is the case. Populations of both white sucker and brown bullheads in the Harbour have an unusually high prevalence of cancerous lesions of the skin (papillomas), liver (hepatomas) and other tissues (Cairns and Fitzsimons 1986). Since young white suckers live in streams, migrate out of the Harbour as they grow, return only to spawn and do not exhibit lesions until at least four years of age, it could be argued that the causal agent was not associated with the Harbour. The same could not be said for bullheads. They are relatively sessile, spending the majority of their life in and around the Harbour. Similar lesions have been observed in brown bullheads from the Black River, an Ohio tributary to Lake Erie highly contaminated with PAH from industry (Baumann 1984; Baumann et al. 1982). However, levels of specific PAHs in both sediments and fish were generally about ten times those in Hamilton Harbour, and the relative proportions of each compound differed. Skin lesions could be induced in laboratory populations by painting their backs with extracts of sediments taken from the Black River.

The ecological significance of cancer in fish has yet to be demonstrated. However, whether or not productivity of fish populations is affected, the presence of both PAH compounds and cancers in fish provides a clear indication of environmental degradation. A further consideration should also be human health. There are no guidelines describing the acceptable level of PAH compounds in edible portions of fish and no studies of how the levels in fish compare to the levels in edible portions induced by common smoke curing processes. These questions need to be addressed if a sports fishery becomes established on the Harbour.

4.2.13 POLYCHLORINATED BIPHENYLS

The effects of PCBs on aquatic biota may be derived from exposure to waterborne, sediment and dietary sources (Rubinstein et al. 1984) but most data on toxicity and accumulation were derived from experiments using waterborne exposure. For algae, reduced growth and changes in population structure occurred at levels as low as 0.1 µg/L while acute lethality of freshwater invertebrates and fish should occur at levels as low as 1.3 µg/L and 8 µg/L respectively (Eisler 1986b). Acute toxicity increases with exposure time and also varies with the formulation (percent chlorination) and species tested.

Sublethal and chronically toxic effects on invertebrates involve reduced growth rates and decreased shell growth of crustaceans at levels ranging from 1 to 20 µg/L. Growth of fish was also reduced at levels near 1.0 µg/L and the threshold concentrations for reproductive failure were 0.1 - 1.0 µg/L. Concentrations of PCBs in fish eggs of 0.3 - 2.0 mg/kg are associated with reduced survival and increased prevalence of deformities in newly hatched fry, the degree of effect again being a function of species tested and the PCB formulation. These kinds of effects were also associated with elevated PCB concentrations in gonads (24 mg/kg) and whole body (0.4 mg/kg) of parent fish.

Physiological responses are also seen. PCBs interact with hepatic mixed function oxidases of trout to reduce carcinogenesis of aflatoxin, even though PCBs induce elevated activities of these enzymes. In contrast, PCBs inhibit the Na-K ATPases of fish and reduce plasma thyroxin levels, thus impairing the ability of migratory salmonids to adapt to seawater. Prolonged dietary exposures inhibited growth, enlarged livers, changed muscle water content and lowered muscle lipid. Anemia, hyperglycemia, impaired ion regulation and impaired muscle control are also evident as is disruption of collagen metabolism and backbone development. To protect aquatic biota, the estimated 'safe' concentration of PCB in water is roughly 0.1 to 1.0 µg/L.

For the most part, PCB levels in Hamilton Harbour do not appear dangerous when compared to these criteria. Observations of waterborne concentrations as high as 90 µg/L in Windermere Basin far exceed the threshold for chronic toxicity, assuming that all PCB is freely available, but these observations are rare and likely due to short-term sediment resuspension. Average levels were less than 0.02 µg/L, below the threshold for chronic toxicity. The relatively low levels of PCB in fish suggest that not all PCBs are taken up and/or that the elevated levels occur only for very brief intervals. An alternate possibility is exclusion of fish from zones where PCB levels are high but water is anoxic. Elevated levels of PCB in birds and turtles suggests food chain accumulation but, for birds, it is likely that there is a source outside the Harbour.

4.2.14. OTHER CHLORINATED ORGANIC CHEMICALS

Since the sum of all chlorinated organics is close to the water quality objectives for individual chemicals (IJC 1978), it is unlikely that toxic levels of any are toxic by themselves.

4.2.15. MIXTURES

The presence of each chemical in Hamilton Harbour should not be considered in isolation. Many chemicals are discharged simultaneously in effluents so that short-term elevations in one should be associated with elevations of others. Mixture effects have been most studied with metals. There are three possible general interactions: simple additivity, in which the toxicity of a mixture of chemicals is equal to the sum of the toxicities of the components; less-than-additivity, in which the mixture toxicity is less than predicted from a simple summation; and more-than-additivity, in which the toxicity exceeds a simple summation (one or more components have become more toxic).

Hodson et al. (1979) provide a good illustration of the complexity of the mixture question in their review of copper. Copper has shown less-than-additive acute toxicity with a nonionic detergent and malathion (organophosphate pesticide), additive toxicity with phenol, zinc, ammonia, zinc and phenol, and zinc and nickel, and more-than-additive toxicity with an anionic detergent, cadmium, zinc, zinc and cadmium, parathion, and sevin (organophosphate insecticides).

These data suggest that there are few concrete generalizations, probably because the experimental methods varied considerably between studies. For acute lethality, mixture effects were successfully predicted in a river contaminated by metals and phenols when simple additivity was assumed (Brown and Dalton 1970). However, this concept has not been well tested for sublethal or chronic exposures where adverse effects may be the product of completely different modes of toxicity. Nevertheless, the IJC has published a rationale for evaluating mixtures which assumes additivity of the sublethal responses that formed the basis for objectives (IJC 1981). While based on a very weak assumption, the rationale provides a mechanism for identifying occasions or places where mixture effects might be likely. The component that would contribute most to any mixture effects can also be identified.

Since the publication of that rationale, research on structure activity relationships (SARs) has demonstrated that chemicals related by an SAR show additive toxicity in acute and chronic tests with bacteria, Daphnia, and guppies (Hermens et al. 1984a; b; 1985a; b). The theory is that compounds related by SARs share a common mode of toxicity, and additivity was shown for mixtures of up to 50 compounds.

Wong et al. (1978) tested the toxicity to algae of 10 metals, mixed at concentrations equal to the Great Lakes Water Quality Objectives. Photosynthesis and population growth rates of test algal cultures, exposed in a medium resembling lake water, were greatly reduced by this mixture and by the mixture diluted to 1/10. Photosynthesis was also inhibited by up to 78% when the medium was Hamilton Harbour water. While much of the toxicity could be accounted for by zinc, since zinc alone at the objective level appeared toxic, there was still some residual mixture effect (Wong, personal communication).

A similar experiment was performed with fathead minnows, rainbow trout, and Ceriodaphnia dubia (Spehar and Fiandt 1986). Acute and chronic toxicity tests were conducted with single metals (arsenic, cadmium, chromium, copper, mercury, and lead) at concentrations calculated from the U.S. EPA method for estimating criteria. Acute lethal tests were conducted at the estimated maximum allowable concentration, and chronic tests were conducted at the average allowable concentrations. The six metals mixed together were acutely lethal to all tested rainbow trout and Ceriodaphnia at the maximum allowable concentration; fathead minnows were somewhat more resistant, dying only at four times the maximum allowable level. Using the single metal toxicity tests as a reference, the individual contributions to mixture effects appeared more-than-additive for fathead minnows and slightly less-than-additive for Ceriodaphnia. For chronic toxicity tests, mixture effects based on growth and reproduction were strictly additive for Ceriodaphnia and less-than-additive for fathead minnows. Toxicity to Ceriodaphnia was observed at mixture concentrations equivalent to one-third the recommended level.

It is clear that mixture effects cannot be simply predicted, since the interactions are not consistent. It is also clear that chemicals cannot be considered in isolation. The simple application of the additivity concept may provide some useful estimates of toxicity, but they cannot be relied upon for accuracy; there is little experience measuring mixture effects in real systems. Since each chemical will interact with complexing materials due to differences in binding constants and partition coefficients, the degree of exposure to each component of a mixture will not be the same as in a laboratory exposure.

5.0 DISCUSSION

Hamilton Harbour is extensively contaminated with nutrients, organic wastes and chemicals discharged from municipal and industrial sewers. Levels of metals in Harbour sediments increased from the 1800's to the present in parallel to the increasing activity of industries and the size of the City's population (Figure 5). It is logical to assume that similar increases occurred in the input of other chemicals and organic wastes from early textile, steel, and metal fabricating industries and from domestic sewage. Hamilton did not treat its sewage in the early 1800's, relying on water closets and, after 1854, direct discharge of sewage to the Harbour. The result was poor sanitation, cholera epidemics and gross pollution of the Harbour.

The historical sediment record also indicates a decrease in metal inputs since the late 1960's, a trend echoed in numerous surveys by the Ontario Ministry of the Environment. Reductions in the input of iron and phenol by more than 90% since 1965 exemplify these improvements, primarily due to improved waste treatment by industries, diversion of industrial wastes to the Hamilton Wastewater Treatment Plant (WTP), and improvements in design, capacity and operation of WTP's in Hamilton, Burlington and Dundas.

Despite these improvements, pollution of the Harbour remains. Storm sewer separation in Hamilton is incomplete and municipal and industrial discharges to the Harbour generate unacceptable conditions. Chemical contamination is primarily a product of the steel industries, with municipal WTPs contributing the next largest share (Tables 31 and 32). Levels of

Table 31 Estimated total loadings (kg/d) of metals and cyanide summarized from previous tables and text. Most data are from 1985 but earlier figures (to 1978) were included where recent data were unavailable. A blank indicates that no data were available.

SOURCE	IRON	ZINC	LEAD	NICKEL	CADMIUM	CHROMIUM	COPPER	ARSENIC	MANGANESE	CYANIDE
Industry	5256	128	64			36	96		202	65
WTPs	201	36	1.9	11.3	0.8	5.9	7.3		28	
Tributaries	1130	26	15		2.6	10.0	9.3		104	0
Storm Sewers	89	9.8	2.7	2.0	0.3	1.9	1.3	0.04	10	1.0
Atmospheric[1]	0.03	0.02	0.007	0.0007			0.007			
TOTAL	6676	200	81.7	11.5	3.7	53.8	113.9	0.04	344	66.1
PERCENT CONTRIBUTION TO TOTAL LOADINGS										
Industry	78.7	64.0	78.6			66.9	84.3		58.7	98.5
WTPs	3.0	18.0	2.3	98.3	21.6	11.0	6.4		8.1	
Tributaries	16.9	13.0	15.8		70.2	18.6	8.2		30.2	
Storm Sewers	1.3	4.9	3.3	1.7	8.1	3.5	1.1	100.0	2.9	1.5
Atmospheric[1]	0.0005	0.01	0.01	0.006			0.006			
TOTAL	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[1] Rainfall Only, Chan 1986

Table 32. Estimated total loadings of organic chemicals summarized from previous tables and text. Most data are from 1985 but earlier figures were included where more recent data were unavailable.

SOURCE	TOTAL PCBs kg/a	TOTAL PAHs kg/a	TOTAL PESTICIDES kg/a	PHENOLS kg/d	OIL & GREASE kg/d
Industry		639		34	2596
WTPs	5.5	7.3	8.6		
Tributaries				0.9	
Storm Sewers	8.3		5.7	1.1	
Atmospheric[1]	0.228		0.359		
Spills					1
TOTAL	14.0	646.3	14.7	36.0	2597
PERCENT CONTRIBUTION TO TOTAL LOADINGS					
Industry		98.9		94.4	100.0
WTPs	39.2	1.1	58.7		
Tributaries				2.5	
Storm Sewers	59.2		38.9	3.1	
Atmospheric[1]	1.6		2.4		
Spills					0.03
TOTAL	100.0	100.0	100.0	100.0	100.0

[1] Rainfall Only.

waterborne and sediment metals are much higher near these sources than in other areas of the Harbour (Table 12; Figs. 4 & 6). There is also significant contamination by pesticides and PCBs from combined sewer overflows and from tributaries draining urban areas of Hamilton, Dundas, Burlington and Waterdown.

Chemical loadings to the Harbour, relative to other loadings to Lake Ontario, are quite high for iron; for PCBs, loadings are moderate relative to sources such as the Niagara River (Table 33). This, however, is a biassed

Table 33. Chemical loadings in Hamilton Harbour relative to other Lake Ontario sources.

Chemical	To Hamilton Harbour[1]	From Hamilton Harbour to Lake Ontario[2]	From Niagara River to Lake Ontario[2,3,5]	From Atmosphere to Lake Ontario[2,4]
METALS (kg/d)				
Arsenic	0.04		395	
Cadmium	3.7		590	
Chromium	53.8		890	
Copper	114	23.3	1123	260
Iron	6676	657	217534	1731
Lead	82	16	548	1038
Nickel	11.5	16	1036	
Mercury			11.7	
Zinc	200	65.7	1671	2597
ORGANICS (kg/a)				
PCBs	14	< 24	3050	56
Total Pesticides	14.7	15	2516	96
Total PAH	646	180-1050	44384	8100
ORGANICS (kg/d)				
Oil and Grease	2597			
Phenols	36			
Cyanide	66			

1 Estimated loadings for 1985 calculated from data in tables of this report.

2 MOE 1986e; Poulton 1987

3 MOE 1985

4 calculated from Strachan and Huneault 1979

5 Data Interpretation Group 1986, dissolved fraction only

Table 34. Chemical levels (µg/L) in Hamilton Harbour water compared to other Lake Ontario locations.

Chemical	Hamilton Harbour[1]	Lake Ontario		IJC Water Quality Objective[5]
		Near Hamilton[2]	Offshore[3,4]	
METALS				
Arsenic	1		0.55	50
Cadmium	0.3		0.05	0.2
Chromium	6		0.55	20
Copper	3.5	4.4	1.3	5
Iron	220	37	21.8	300
Lead	5		0.39	5
Nickel	10		1.65	25
Mercury	0.04		0.025	0.2
Zinc	30	4.7	1.2	30
ORGANICS (kg/a)				
PCBs	< 0.02	0.0031	0.00043	0.001
Total Pesticides	0.012	0.0103	0.0105	0.001-0.006
HCB	< 0.001	0.000068	0.000036	0.01
Oil and Grease	0.42	0.40		
Phenol	< 1			

1 Mean values from tables within this report for all areas for 1984 with the exception of PCB, pesticides and HCB (1982) and oil and grease (1972).

2 Mean values for samples taken at several depths within a 6 km radius of the Burlington canal (MOE 1986e).

3 IJC 1983; Biberhofer and Stevens 1987.

4 Strachan and Edwards 1984.

5 IJC 1977.

assessment, since it reflects past analytical capabilities rather than current environmental priorities. There are virtually no data on chemicals such as chlorinated dioxins and furans because the technology for their measurement is so new that its application is not widespread. More than 100 organic chemicals that are not routinely measured have also been detected in surveys of effluents from steel mills and the Hamilton and Burlington WTPs (Tables 16 and 18). While those from the steel industry would be treated and the majority of others would be degraded quickly, it is likely that chlorinated compounds, PAHs, furans and phthalates could have environmental impacts.

The number of hazardous compounds may be even higher, considering that the analyses covered few samples, and that effluents from the Dundas and Waterdown WTPs, and combined sewer overflows were not included. Therefore, while the significance of the known chemicals can be evaluated, research is required to describe the full extent of chemical loadings and contamination of the Harbour.

5.1 METALS

The majority of metal loadings are from the steel industries; their contributions range from 59 to 84%, depending on the metal (Table 31). The next largest source is generally tributary loading, due to high volumes of water containing low concentrations. WTPs contribute only a small amount, with the exception of zinc and cadmium. As a result of this loading pattern, levels of metals in sediments and water are highest in the south shore area around the steel industries. While the average concentrations in water meet IJC Water Quality Objectives, they are elevated above background levels in Lake Ontario by 2 - 15 times (Table 34) and objectives are frequently exceeded for copper (>5 µg/L) and zinc (>30 µg/L). The increases over objectives, while frequent, are generally not large, probably due to efficient mixing, and high levels of total organic carbon may mitigate toxicity to most biota through complexation. However, toxicity to algae of metal mixtures at concentrations equivalent to water quality objectives has been observed experimentally in Hamilton Harbour water (Wong *et al*. 1978). Hence, periodic reductions in primary productivity are possible.

Sediment levels of metals exceed dredge spoil disposal guidelines for arsenic, cadmium, chromium, copper, iron, nickel and zinc. Relative to offshore surficial sediments, only iron and zinc levels appear elevated since both surficial offshore and Harbour sediments have higher levels of all metals than 'background' sediments (i.e. sediments deposited before 1800) (Figure 5, Table 35). Compared to other Harbours on Lake Ontario, average levels of cadmium, chromium, copper, nickel and zinc are elevated. The levels in most Harbours, therefore, are below those in offshore sediments, probably because they are shallow and turbulence prevents settling and accumulation of particulates. In contrast, Hamilton Harbour is deep (up to 20 m) and more closely resembles the open lake.

Table 35. Chemical levels (µg/g dry weight) in Hamilton Harbour sediments compared to other Lake Ontario locations.

Chemical	Hamilton Harbour[1]	Other Lake Ontario Harbours[2]	Lake Ontario			Dredge Spoil Disposal Guideline[7]
			Near Hamilton[3]	Offshore[4,5] Background	Surface	
METALS						
Arsenic	12	15[6]	5.9		3.3*	8
Cadmium	3.0	< 0.5-0.8	1.1	4	2.5*	1.0
Chromium	181	16.6-53.3	70.8	119	187	25
Cobalt	17		3.9	24		
Copper	88	4.4-44.3	33.2	44	98	25
Iron	71,900		30,270	45,500	40,200	10,000
Lead	216	1.8-348	42	30	220	50
Nickel	44	2.4-24.9	20.3	91	136	25
Mercury	0.12	0.02-0.44	0.06	0.07	2.35	0.30
Vanadium	62					
Zinc	1,546	18.8-212	138	105	477	100
Cyanide						0.10
ORGANICS						
PCBs	0.33	0.01-0.62	.031		0.058*	0.05
Total DDT	0.006	0.002-0.03	.008			
Total, other pesticides	0.012		<.001-004	0.006		
Total PAH	29.7		0.03-4.61	0.131	0.38-2.69!	
HCB	< 0.001		< .001	0.1		
Oil and Grease	6,107	< 60-2435	846			

1 Mean values for all areas for 1985 with the exception of mercury and cadmium (1975), pesticides (1982) and oil and grease (1973). All means were calculated from data in tables of this report.

2,4 Values for Harbours and offshore Lake Ontario are derived from Thomas and Mudroch (1979) based on a 1978 survey of Harbours, a lake sediment survey by Mudroch and Sandilands (1979) and sediment samples collected between 1968 and 1971. Values marked with an * are from these earlier samples. Values marked with a ! are from the 1970's (IJC 1983)

3 Values for Western Lake Ontario are means of samples taken within a 6 km radius of the Burlington Canal (MOE 1986e)

5 Strachan and Edwards 1984.

6 Bay of Quinte (Canviro 1986)

7 Holmes 1986

One problem with this comparison is that sediments dredged for analysis will include more than the surficial layer, i.e. there will be unknown amounts of old (clean) and new (contaminated) sediment in each sample. Since the surficial layers are highly contaminated (Nriagu et al. 1983), the actual concentration to which benthos are exposed is unknown.

The biological availability and toxicity of sediment metals has not been adequately tested. Analyses of attached filamentous algae suggested elevated levels of copper, chromium and nickel relative to sediment concentrations (Mudroch and Sandilands 1979). Cobalt, zinc, and lead in algae were at levels lower than in sediments and it was not clear whether algae were contaminated with sediment particles. The density of benthic invertebrates, another indication of sediment quality, is reduced in areas of high sediment metal contamination, but these areas are also contaminated with organic chemicals and are often oxygen depleted (Portt et al. 1988).

Studies of blood lead levels have demonstrated little difference between Hamilton Harbour fish and those from other parts of the Great Lakes. In fact, fish from Toronto Harbour and other Lake Ontario locations were somewhat more contaminated (Hodson et al. 1983). This was true even for benthic feeding species which generally accumulate more lead than pelagic feeders. While this suggests that sediment metals are no more available than elsewhere, it may also mean that fish are excluded from areas of highly contaminated sediments by low dissolved oxygen levels.

Disturbance of sediments by dredging could increase the exposure of aquatic biota to metals. Yellow perch (Perca flavescans) exposed to dredged sediments showed significantly higher concentrations of arsenic, chromium and iron (Seelye et al. 1982). The levels of Harbour sediment contamination suggest that studies of dredging effects on fish contamination should precede any major dredging projects. The levels of contaminants currently in sediments require a confined disposal within berms rather than open water disposal; sediment contaminants exceed most guidelines for open water disposal (Table 35; Holmes 1986). The effects of dredging on biota in the Harbour may include changes in physical habitat (e.g. removal or smothering of substrate), reduced dissolved oxygen levels and releases of chemicals. However, Holmes (1986) concluded that there was insufficient information to determine whether current maintenance dredging was having any chemical effects on biota.

Levels of mercury in the edible portion of fish are below the Provincial criteria for consumption (0.5 µg/g wet wt) (Table 36), but there is little data to suggest that large amounts of mercury have ever entered the Harbour. Other metals in the muscle of fish were also at low concentrations, although few fish have been tested. Nickel, lead and cadmium were below the detection limits of the methods employed but these low levels are not surprising, since accumulation in muscle is generally low relative to other fish tissues. Copper and zinc were measureable, but within the range found in fish species from other locations; concentrations of these nutrients in tissues are regulated and are only increased when the fish are exposed continuously to relatively high levels in water. The levels of arsenic and manganese in fish are difficult to assess since few data are available on their levels in fish from other locations.

Mercury levels in gulls from the Harbour were higher than in gulls from other locations; given their ability to feed outside the Harbour, the significance of these levels is also difficult to judge. Gulls also showed much higher levels of other metals relative to fish, suggesting either exposure from sources other than Hamilton Harbour or differences in diet and metal metabolism that affect accumulation rates.

Table 36. Chemical levels in Hamilton Harbour biota compared to other Lake Ontario biota. All concentrations are µg/kg wet weight. (Data from Tables 14 and 29 and Whittle 1986)

Chemical	Fish Species	Hamilton Harbour	Lake Ontario	Year
PCB	Lake Trout (Age 4+)		3670	1981
	Rainbow Smelt		900	1981
	Various Species	24-489		
Hg	Lake Trout (Age 4+)		160	1981
	Rainbow Smelt		70	1981
	Various Species	30-320		

5.2 ORGANIC CHEMICALS

'Oil and grease' is the largest volume organic material discharged to the Harbour (2600 kg/d, Table 33). It settles to the bottom and Harbour sediments are far more contaminated than those of other harbours (Table 35). Oil and grease is released in relatively low concentrations but in high volume effluents, and has little direct toxicological significance. However, it acts as a carrier for other lipophillic persistent organic compounds, so that areas of the Harbour contaminated with oil and grease are also contaminated with more toxic organic chemicals. These areas are generally those closest to the steel mills, the source of more than 98% of total loadings.

The second and third ranking chemicals are phenols (38 kg/d) and PAHs (646 kg/a), also discharged from the steel mills (>95%). While these volumes appear large, they are much less than previously lost in effluents. Phenol discharges have decreased by 96% since 1965 and levels in the Harbour are now below detection limits (1 µg/L); previously average levels had been as high as 10 - 50 µg/L. The current levels of phenols represent no threat to aquatic biota.

The loading of all pesticides together (the sum of DDT and metabolites, chlordane, dieldrin and other chlorinated insecticides) is about 15 kg/a, equivalent to the total PCB loadings (Table 32). The sources of pesticides are primarily WTPs and storm sewers while the most important additions of PCBs seem to be from an unknown source to Windermere Basin and storm sewers draining an industrial property where transformers were once manufactured. Hence, high levels of PCBs have been measured in the water (up to 90 µg/L) and sediments in the Basin and near the Strathearne Slip. Average levels, however, are less than 0.02 µg/L. This level is difficult to compare to samples taken elsewhere, since the detection limit for surveys of Lake Ontario is apparently lower (Table 34). Concentrations of pesticides in the Harbour's water are equivalent to those in Lake Ontario and within the range of objectives for a variety of pesticides (Table 34).

Elevated levels of PCBs have also been observed in the sediments along the north shore, particularly around the LaSalle Park Pier; the source is unknown. On average, PCBs in sediments are about 0.3 µg/g dry weight, a value within the range for sediments of other Harbours on Lake Ontario (0.01 - 0.62 µg/g), but well above the levels in sediments offshore (0.058 µg/g) (Table 35). The levels of pesticides in sediments are quite low; DDT, for example, averages about 0.006 µg/g dry weight compared to 0.002 - 0.03 µg/g in other Lake Ontario Harbours.

The consequence of contamination by persistent chlorinated organics is accumulation in biota. Benthic worms in Windermere Basin contained 2 - 6 times more PCB, chlorinated pesticides and hexachlorobenzene (HCB) than did the sediments they were associated with. While fish have accumulated these compounds, the levels in edible portions (muscle) have declined steadily between 1972 and 1981 and have been lower than observed in fish from Lake Ontario (Table 36). However, this comparison may not be valid since different species are involved. A large portion of the species tested from Hamilton Harbour were benthic feeders, which presumably would be most exposed to sediment chemicals. Nevertheless, the levels were low enough that edibility was unaffected.

In contrast, eggs from fish-eating colonial birds that nest in Hamilton Harbour contain extremely high levels of chlorinated organic compounds. While levels have declined steadily since the early 1970s, they are still many times higher than in the muscle of fish. While this may represent a further step in food-chain biomagnification of these compounds within the Harbour, it is also possible that there is a more important source outside the Harbour, since the birds can range widely. Terns increase their body burdens of chlorinated organic chemicals after migrating to breeding sites on the Harbour (Gilbertson and Reynolds 1972). Since these sites are adjacent to the sand bar separating the Harbour from Lake Ontario, the source of chemicals to the birds may be fish caught in the lake rather than in the Harbour.

The eggs of snapping turtles are also quite contaminated (Table 28), possibly because turtles accumulate chemicals for 19 years before they first reproduce. With the exception of PCBs, the concentrations of chlorinated organics are much lower than in birds, implying a local source of the PCBs in both organisms. Therefore, PCBs appear to be available to aquatic food chains, probably via the sediments.

PAH compounds are probably the most important toxic chemicals released to the Harbour, in that volumes are quite high and the class includes many compounds considered carcinogens. The loading rate from effluents is equivalent to about 646 kg/a, compared to 8100 kg/a loaded to all of Lake Ontario from the atmosphere (Table 33).

Levels of PAH in water are rarely reported since PAHs are usually quite insoluble. However, concentrations in particulates of 3.3 - 5.5 µg/g (MOE 1986c) have been measured and the majority of this material is precipitated to the sediments or washed into Lake Ontario (see section 5.3 on "Impact on Lake Ontario"). In 1985, the sum of 12 PAH compounds in one sediment sample equalled 29.7 µg/g dry weight, a value lower than in previous samples but 10 - 100 times the levels found in sediments of offshore Lake Ontario.

PAH compounds are rarely measured in fish tissues because fish can metabolize and excrete them quickly. However, in 1978, the sum of four PAH compounds in carp from Hamilton Harbour was 0.27 µg/g wet weight (about 1.0 µg/g dry weight), more than 100 times the levels found in carp from the Detroit River (Table 30). For pike from Hamilton Harbour, the levels were lower than in carp and only about 1.5 - 3 times higher than in pike from the Detroit River at the mouth of the Rouge River. While the two ecosystems are not strictly comparable, each species should occupy similar habitat in both areas and be similarly exposed to sediment contamination from heavy industry and urban development.

5.3 IMPACTS ON LAKE ONTARIO

Chemical loadings from the Harbour to the Lake are fairly high relative to inputs from the atmosphere or the Niagara River (Table 33). Atmospheric inputs represent the transfer of dust and air pollutants via rain and dustfall to the lake's surface. While concentrations are low, the total volume of rain over the surface of the lake is quite high. The Niagara River is the largest single source of water to Lake Ontario. It carries dissolved and particulate-bound chemicals transferred from Lake Erie or added by effluents from numerous industries, municipalities and waste dumps along the course of the river.

For metals such as chromium, copper, iron, lead, and zinc, and organic chemicals such as PAH, the inputs to Lake Ontario from the Niagara River are about 5 - 100 times the amounts discharged directly to Hamilton Harbour. The transfer of chemicals from the Harbour to Lake Ontario are generally lower, however, suggesting that the Harbour acts as a chemical trap. For zinc, total loadings from the Niagara River are only 25 times greater than those from the Harbour (Table 33), despite river flows at least 150 times greater than the outflow from the Harbour.

For other chemicals such as PCBs and pesticides, the loadings to Lake Ontario via Niagara and the atmosphere far exceed those from Hamilton, a reflection perhaps of the nature of industries in the Niagara Region.

The figures in Table 33 for transfers from Hamilton Harbour to Lake Ontario may be overestimated. They were calculated simply from the total outflow of water from the Harbour multiplied by the average concentrations of chemicals in the water column (MOE 1985). As MOE (1986e) demonstrated, estimates of net loading can be seriously changed by simultaneously considering inflow from the lake and outflow to the lake when the canal is stratified. Under these conditions, there are flows in opposite directions on the surface and bottom of the canal, so that chemicals are entering the Harbour as they are leaving. Calculation of net loadings can be biassed by mixing within the Harbour and the lake and by the location and depth of sampling stations.

MOE (1986e) reported studies of Western Lake Ontario near Hamilton that demonstrated detectable plumes of Harbour water during summer months in a zone within a radius of 6 - 7 km from the Canal (the limits of the study). This plume is pushed and diluted by nearshore currents and by upwelling from deeper parts of the lake. The chemical composition of the plume varies annually due to thermal stratification. Epilimnetic waters flow out of the Harbour in the summer, carrying municipal and industrial effluents without as much dilution from hypolimnetic waters as in the winter; the summer plumes also tend to remain in the epilimnion of the lake. Mixing, dilution and retention within the Harbour should be much greater in the winter.

The consequence of the Harbour discharge is elevated levels of ammonia, metals and other constituents in the lake. Copper levels exceeded water quality objectives in 26% of samples within 6-7 km of the canal, and sediment levels of metals were elevated, particularly as water depth increased (MOE 1986e). Levels of PAH, however, did not correspond to the plume distribution, suggesting alternate sources; given the magnitude of other inputs (Table 32) this is not surprising.

The presence of the plume and chemical contamination is associated with some changes in benthic organisms (MOE 1986e). A diversity index of community structure was affected up to 7 km from the canal and there were varying proportions of pollution-tolerant and sensitive species of invertebrates. The samples reflecting pollution exposure were often closest to the canal and there were high proportions of organisms that could metabolize organic material. However, some stations in deeper water offshore had high densities of pollution-tolerant species and high levels of sediment heavy metals, indicating depositional zones for particulates.

5.4 CONCLUSIONS

Despite dramatic improvements in waste treatment, there is no question that Hamilton Harbour receives excessive loadings of toxic chemicals. Relative to the open waters of Lake Ontario, average levels in water, sediment and biota of most chemicals are not elevated. However, the use of averages (in particular geometric means) obscures the extreme values occuring in some water and sediment samples. Part of the Harbour, in particular the south shore and Windermere Basin, are severely contaminated and conditions may even

be lethal to aquatic biota. Other obvious problems are high levels of PAH compounds in all media; PCBs in some sediment samples and in turtles and gulls; mercury, cadmium and lead in gulls; and iron and zinc in sediments. Of these, the most important contaminants are PAHs and PCBs, based on toxicity and persistance. Chemical impact on biota that have already been observed include an absence benthic invertebrates in a 'toxic zone' near industry and, possibly, an elevated prevalence of tumours in fish.

Waterborne levels of chemicals are probably minimized by complexation by inorganic and organic particulates, as demonstrated by high levels of PAH compounds in suspended matter. This would also explain the high levels of chemicals in sediments as the particulates settle to the bottom. While the majority of biota are relatively uncontaminated, it is obvious that low levels of dissolved oxygen near contaminated sediments may prevent access to these sediments and exposure to the chemicals. Therefore, further improvements in waste control and levels of dissolved oxygen in the Harbour could have the unwanted side-effect of increasing levels of chemical contamination of fish and other biota.

Sediment dredging might solve the problem of 'in-place' pollutants, but this solution creates further problems of disposal. This is particularly acute in Windermere basin where dredging is proposed to remove the Harbour's most contaminated sediments. Containment through landfilling adjacent to the Harbour may simply shift the problem without solving it if leaching occurs. Furthermore, even if it prevents contamination of biota, it removes littoral habitat.

This review has demonstrated many areas in which research is required to fully understand and manage chemical contamination. These include research to:

1. identify all sources of PCBs;

2. assess the fate and effects of PAH, particularly their possible role in fish carcinogenesis;

3. identify the types, source and distribution of "non-standard' organic chemicals;

4. determine the biological availability of sediment chemicals and the interaction of availability with oxygen levels in water;

5. determine suitable means of treating sediments in place to reduce biological availability;

6. determine suitable means of disposal of dredge spoil while still preserving habitat for aquatic biota.

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8.0 APPENDICES

8.1 APPENDIX A - GLOSSARY

ABS - Alkyl benzene sulfonate (a non-biodegradable detergent active ingredient).

Aroclor - Trade name of PCB mixtures made at Monsanto.
Bilge water - internal tanker wastes

Ballast water - water in ships ballast or fuel tanks to maintain vessel stability.

CCIW - Canada Centre for Inland Waters

CB - chlorobenzene

CP - chlorophenol

DE - Destruction efficiency

DOFASCO - Dominion Foundry and Steel Company

EPA - Environmental Protection Agency

γ-HCH - gamma-hexacyclohexane = lindane, a pesticide

IJC - International Joint Commission

MOE - Ontario Ministry of the Environment

NWRI - National Water Research Institute

OWRC - Ontario Water Resources Commission

PAH - Polynuclear aromatic hydrocarbon

PCB - Polychlorinated biphenyl, an industrial dielectric agent

PCDD - Polychlorinated dibenzo-p-dioxin or dioxin

PCDF - Polychlorinated dibenzofuran or dibenzofuran

QEW - Queen Elizabeth Way highway

SWARU - Solid Waste Reduction Unit, garbage incinerator in Hamilton

STELCO - Steel Company of Canada

WTC - Wastewater Technology Centre, Part of CCIW.

WTP - Wastewater Treatment Plant